Eur. Phys. J. D **43**, 109–112 (2007)
DOI: 10.1140/epjd/e2007-00075-y

THE EUROPEAN PHYSICAL JOURNAL D

Changing the fragmentation pattern of molecules in helium nanodroplets by co-embedding with water

Y. Ren, R. Moro, and V.V. Kresin[a]

Department of Physics and Astronomy, University of Southern California, Los Angeles, CA 90089-0484, USA

Received 23 July 2006
Published online 24 May 2007 –

Abstract. Individual amino acid molecules embedded in helium nanodroplets fragment extensively when the beam is ionized by electron bombardment. However, we find that when glycine and tryptophan are picked up right after, or right before, a small amount of water, the mass spectra become significantly altered. For glycine, the detected ions consist almost entirely of intact protonated amino acids, with or without a few water molecules attached. In other words, the presence of water exerts a striking "buffering" effect on the ionization-induced fragmentation. For tryptophan the effect is weaker but also present. In both cases, the hydroxyl group lost upon ionization overwhelmingly comes from the water partner (in strong contrast to the situation observed when amino acids are picked up by neat water clusters). A complementary experiment involving DCl molecules co-embedded with water shows that in this case Cl and/or DCl invariably leave the droplet upon ionization. The observed patterns may be steered by the analytes' dipole moments or by solvation effects.

PACS. 36.40.Qv Stability and fragmentation of clusters – 34.80.Ht Dissociation and dissociative attachment by electron impact

1 Introduction

A perpetual issue in mass spectrometry is molecular fragmentation, e.g., as a result of electron impact ionization. One of the techniques emerging to explore and possibly counteract this effect is to attach the analyte species to an atomic or molecular cluster, or to embed it inside a cluster, and to perform mass spectrometry on the resulting agglomerate.

Probably the most prevalent cluster beam pick-up scheme today is that employing liquid helium nanodroplets [1,2]. From the beginning of helium nanodroplet isolation studies, there was hope that embedding molecules in the middle of these "balloons" would enable fragmentation-free mass spectrometry of fragile species. However, things turned out to be not so simple. When the system is probed by electron bombardment, the ionization of impurities proceeds primarily via charge transfer to the embedded species from a positive He^+ hole hopping through the droplet (see, e.g., [3–5]). The accompanying energy release is substantial, and can result in extensive fragmentation of the impurity [6]. For example, it has been found that glycine (Gly, the lightest amino acid), and tryptophan (Trp, the heaviest) molecules embedded in He_n survive ionization only marginally better than free gas-phase molecules [7–9], see Figure 1A.

[a] e-mail: kresin@usc.edu

Motivation for the present work came from our recent studies of amino acid and water molecules adsorbed on water clusters in a beam [10], in which it was observed that upon electron bombardment ionization, fragmentation of the complex was limited only to hydroxyl group loss. Interestingly, there was a strong tendency (≈60% for Gly, 30% for Trp) for this group to come from the guest molecule rather than the host cluster. That is to say, the amino acid fragmentation channels are completely different when the molecules are adsorbed on water clusters than when they are free or embedded in He droplets. It was natural to inquire what would be observed if the doping arrangements were, in a fashion, combined by sequentially embedding water molecules and amino acids in a He_n beam. Complementary measurements were also made with a simple acid, DCl.

2 Experimental arrangement

A beam of ^{4}He nanodroplets is produced by the standard low-temperature supersonic expansion method, using a 5 μm orifice maintained at 14 K and 40 bar gas stagnation pressure. These conditions were fixed to match those in reference [7], and correspond to an average droplet size of 10^4 atoms [1].

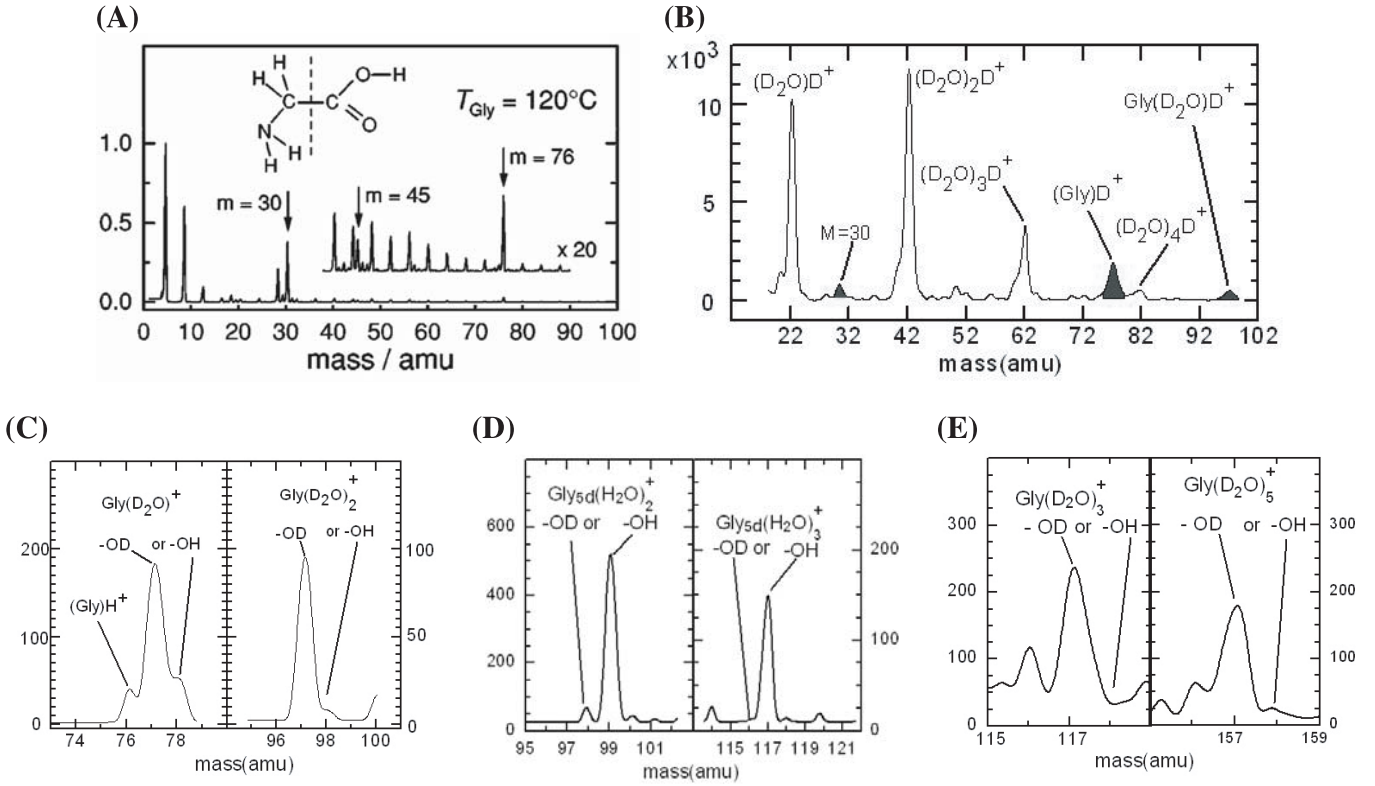

Fig. 1. (A) Mass spectrum of He droplets doped with Gly molecules obtained by electron-impact ionization (from Ref. [7]), showing a fragmentation picture very similar to that of free Gly [9]: the major fragment peaks are $NH_2CH_2^+$ (30 amu) and $COOH^+$ (45 amu) resulting from C-C bond cleavage, with practically no signal at the parent mass, 75 amu. The 76 amu $GlyH^+$ peak has been assigned to a protonated fragment of a larger glycine cluster. We have reproduced this pattern with our setup. (B) Present work: mass spectrum obtained for He droplets picking up D_2O followed by Gly. The most intense peaks result from protonated fragments of $(D_2O)_n$ [15] and from protonated Gly ions. (C) Segments of mass spectra corresponding to the situation in (B), showing that OD loss from water is much more probable than OH loss from Gly. (D) Same for pick-up of regular water followed by deuterated Gly. Again, the loss of OH from water dominates over OD loss from Gly-d5. (E) Analogous behavior is found when Gly is picked up first, followed by D_2O.

The beam enters the pick-up chamber through a 0.4 mm skimmer, and then passes through a rotating wheel chopper (set to 97 Hz for lock-in detection, see below) followed by two pick-up cells. One is filled with water vapour through half a meter of 0.75 mm I.D. tubing: a double-needle valve connecting the latter to a water-filled container is momentarily opened, and the resulting charge provides water pressure for the duration of a mass spectrum. The other cell contains glycine or tryptophan or DCl [11]. When filled with Gly or Trp powder, the cell is heated up to 105 °C and 190 °C respectively; thermal decomposition is not expected to be strong at these temperatures [10,12]. For DCl the connection is similar to the water vapor case, with a lecture bottle and a regulator taking the place of the water container, and the needle valve kept slightly open.

In the next chamber the droplet beam is detected by a quadrupole mass spectrometer (Balzers QMG 511, 0–500 amu), with an electron impact ionizer set to 77 eV energy for all the data presented here. Feeding the output of the mass spectrometer into a lock-in amplifier synchronized with the beam chopper provides discrimination against background signals.

3 Results

3.1 Water and glycine

To distinguish the hydroxyl group from the water and glycine molecules, we employed isotopic permutations. First, regular glycine (75 amu) was co-embedded with D_2O; then deuterated Glycine-d5 (80 amu) was used with H_2O. As described below, both variants gave consistent results.

Figure 1B shows the mass spectrum corresponding to pick-up of heavy water followed by glycine. It is drastically different from that of Figure 1A: in addition to the well-known series of deuterated water peaks [13–15], the main feature is a peak at 77 amu corresponding to an intact deuterated Gly molecule. The fragment peak at mass 30 is strongly suppressed, and a large part of it is believed to come from solitary embedded glycine anyway (since otherwise one would expect to see prominent peaks at 50, 70, 90 amu corresponding to the 30 amu fragment ion with heavy-water molecules attached).

Figures 1C and 1D show representative portions of the mass spectra in greater detail. They confirm that the

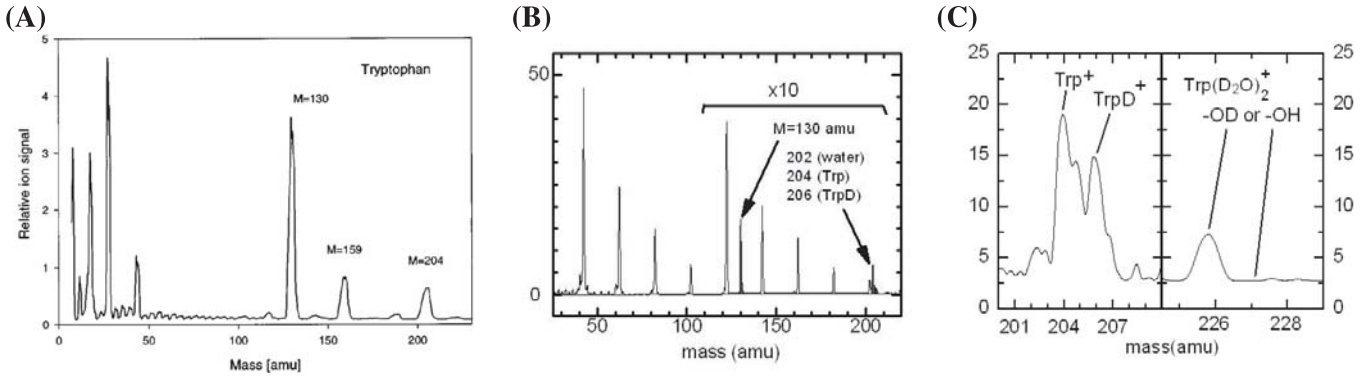

Fig. 2. (A) Mass spectrum of He droplets doped with Trp molecules (from Ref. [8]). (B) Present work: mass spectrum obtained for He droplets picking up D_2O followed by Trp [15]. (C) As in Figure 1, hydroxyl loss comes predominantly from the water partner.

predominant fragmentation product is glycine plus a water cluster (or a fragment of one) minus an OH (or OD) group lost by the latter. This implies that the addition of water to He droplets quenches the fragmentation of glycine. And in strong and interesting contrast with our aforementioned work on pick up by pure water clusters [10], here the hydroxyl group overwhelmingly comes from the water, not the glycine.

We also performed an experiment exchanging the water and glycine pick-up sequence. Figure 1E illustrates that the hydroxyl loss asymmetry remains the same.

3.2 Water and tryptophan

Pick-up of heavy water followed by tryptophan does not appear to buffer Trp fragmentation as dramatically as in the case of glycine, but does reduce it: compare Figures 2A and 2B and once more note that part of the 130 amu peak in Figure 2B actually comes from solitary embedded Trp [16]. Figure 2C shows that protonated ions here again derive from hydroxyl loss by the water molecule or cluster rather than by the amino acid.

3.3 Water and DCl

As a complementary strong-acid species, we also looked at the electron impact ionization products of He clusters doped with H_2O followed by DCl. The mass spectra were found to contain strong (protonated) water cluster peaks [cf. Fig. 1A], plus a minor $(H_2O)_nD^+$ signal, but no trace of a chlorine atom. This was confirmed by a D_2O+DCl pick-up experiment. Thus ionization-induced fragmentation in this case consists of two channels: dominantly complete DCl loss plus a small amount of Cl atom loss. This reveals that the He^+ ion has a much higher probability to impact DCl than an amino-acid molecule.

For comparison, pure $(H_2O)_nHCl$ and $(H_2O)_nDCl$ clusters have been found to universally lose their chlorine atom upon electron-impact ionization [17,18].

4 Discussion

We see that for amino acid analytes inside a helium droplet, an adjacent water cluster dramatically restructures their fragmentation pattern and serves as a potent "buffer". Further research is desirable to clarify the origin of such a strong effect; some speculative considerations are discussed below.

It is expected that the water and acid impurities submerge in helium and meet inside the droplet. It is not obvious what degree of bonding and solvation takes place upon their encounter. If solvation is minimal, as is possible in this cryogenic environment, the amino acid molecules will park themselves near the water complexes, and then our data imply that the latter serve as preferential targets for the migrating He^+. This could be guided, for example, by the relative magnitude of the targets' electric dipole moments: 0.7–0.9 D for the neutral conformation of glycine [19] vs. 1.1–3 D for the water molecule and the smaller ground-state water clusters [20,21] (except for the symmetric tetramer). DCl, on the other hand, possesses a relatively large moment, 1.1 D [22], and that of tryptophan is even larger, ≈2.6 D [23], which may correlate with the fact that we found these molecules to have a higher probability of being impacted in the ionization process. Note that steering of charge migration in a nanodroplet by the multipole electrostatic potential of an embedded impurity has indeed been shown to be a quantitatively appropriate picture [24].

Alternatively, it is possible that the acid molecules "solvate", i.e., work their way in between — and become shielded by — the water molecules even in the helium droplet environment. This resembles the observation [25,26] that during the pick-up process, subsequent water molecules appear to be able to insert themselves into preformed cyclic rings in the droplet. The resulting arrangement may be analogous to that obtained when water is picked up subsequent to the amino acid, and indeed we saw that the mass spectral features turn out to be similar.

The effect reported here may be useful for mass spectrometric studies involving helium nanodroplet isolation.

Spectroscopic measurements of the structure of submerged water-cluster complexes, complemented by studies of ion-molecule charge transfer both in the gas phase and in the droplet environment (cf. Ref. [5]) would help to elucidate the origin of the dramatic reduction of amino acid fragmentation. It would also be interesting to investigate whether other dopants share water's ability to provide such restructuring of the mass spectrum.

This work was supported by the U.S. National Science Foundation under Grant No. PHY-0245102.

References

1. J.P. Toennies, A.F. Vilesov, Angew. Chem. Intern. Ed. **43**, 2622 (2004)
2. F. Stienkemeier, K.K. Lehmann, J. Phys. B: At. Mol. Opt. Phys. **39**, R127 (2006)
3. A. Scheidemann, B. Schilling, J.P. Toennies, J. Phys. Chem. **97**, 2128 (1993)
4. B.E. Callicoatt, D.D. Mar, V.A. Apkarian, K.C. Janda, J. Chem. Phys. **105**, 7872 (1996)
5. M. Fárník, J.P. Toennies, J. Chem. Phys. **122**, 014307 (2005)
6. S. Yang, S.M. Brereton, M.D. Wheeler, A.M. Ellis, Phys. Chem. Chem. Phys. **7**, 4082 (2005)
7. F. Huisken, O. Werhahn, A.Yu. Ivanov, S.A. Krasnokutski, J. Chem. Phys. **111**, 2978 (1999)
8. A. Lindinger, J.P. Toennies, A.F. Vilesov, J. Chem. Phys. **110**, 1429 (1999)
9. NIST Mass Spec Data Center, "Mass Spectra", in *NIST Chemistry WebBook, NIST Standard Reference Database No. 69*, edited by P. Linstrom, W.G. Mallard (National Institute of Standards and Technology, Gaithersburg, 2005), `http://webbook.nist.gov/chemistry`
10. R. Moro, R. Rabinovich, V.V. Kresin, J. Chem. Phys. **123**, 074301 (2005)
11. Glycine was purchased from VWR, deuterated glycine from Icon Services, tryptophan from Aldrich
12. K. Aflatooni, B. Hitt, G.A. Gallup, P.D. Burrow, J. Chem. Phys. **115**, 6489 (2001)
13. M. Lewerenz, B. Schilling, J.P. Toennies, J. Chem. Phys. **102**, 8191 (1995)
14. R. Fröchtenicht, M. Kaloudis, M. Koch, F. Huisken, J. Chem. Phys. **105**, 6128 (1996)
15. The number of picked-up water molecules is given by a Poisson distribution [1], here typically centered at $\langle n \rangle \approx 3$, as evidenced by the maximum at $(D_2O)_2D^+$ in Figures 1B and 2B.
16. Increased background in the spectrum comes from picked-up fragments of diffusion pump oil abundant in this mass range.
17. B.D. Kay, Ph.D. dissertation, University of Colorado at Boulder (1982)
18. R. Moro, R. Rabinovich, V.V. Kresin, J. Chem. Phys. **124**, 146102 (2006)
19. F.J. Lovas, Y. Kawashima, J.U. Grabow, R.D. Suenram, G.T. Fraser, E. Hirota, Astrophys. J. **455**, L201 (1995)
20. M. Yang, P. Senet, C. Van Alsenoy, Int. J. Quantum Chem. **101**, 535 (2005)
21. J.K. Gregory, D.C. Clary, K. Liu, M.G. Brown, R.J. Saykally, Science **275**, 814 (1997)
22. E.W. Kaiser, J. Chem. Phys. **53**, 1686 (1970)
23. R. Antoine, I. Compagnon, D. Rayane, M. Broyer, Ph. Dugourd, G. Breaux, F.C. Hagemeister, D. Pippen, R.R. Hudgins, M.F. Jarrold, Eur. Phys. J. D **20**, 583 (2002)
24. W.K. Lewis, C.M. Lindsay, R.J. Bemish, R.E. Miller, J. Am. Chem. Soc. **127**, 7235 (2005)
25. K. Nauta, R.E. Miller, Science **287**, 293 (2000)
26. C.J. Burnham, S.S. Xantheas, M.A. Miller, B.E. Applegate, R.E. Miller, J. Chem. Phys. **117**, 1109 (2002)