

- Halpern, *J. Catal.*, **74**, 434 (1981).
- "Rotational Energy Distribution in Free Jets of CO<sub>2</sub>", with S. P. Venkateshan and S. B. Ryali, presented at the VIII International Symposium on Molecular Beams, Cannes, June 1981.
- "Clusters as a Source of Error in Molecular Beam Scattering Experiments", with H. Tien, P. J. Gale, and S. B. Ryali, *Chem. Phys. Lett.*, **93**, 213 (1982).
- "Terminal Rotational States in Free Jet Expansion of CO<sub>2</sub> by Infrared Emission Spectrometry", with S. P. Venkateshan and S. B. Ryali, *J. Chem. Phys.*, **76**, 2599 (1982).
- "Further Reflections on the Role of a Mass Flux Gage in the Calibration of Mass Spectrometers for Dimers", with N. Lee, *Rev. Sci. Instrum.*, **53**, 1494 (1982).
- "Collision Kinetics in Gas Dynamics", in "Applied Atomic Collision Physics", Vol. 5, E. W. McDaniel, Ed., Academic Press, New York, 1982, p 349.
- "Rotational Energy Distribution in CO<sub>2</sub> Vibrationally Excited by Collision with N<sub>2</sub>", with S. P. Venkateshan and S. B. Ryali, *Chem. Phys. Lett.*, **92**, 606 (1982).
- "Distribution of Internal Energy in CO and CO<sub>2</sub> Scattered by a Hot Platinum Surface", with D. A. Mantell, G. L. Haller, and S. B. Ryali, *J. Chem. Phys.*, **78**, 4250 (1983).
- "Distribution of Internal Energy in NO Vibrationally Excited by a Hot Platinum Surface", with D. A. Mantell, Y.-F. Maa, G. L. Haller, and S. B. Ryali, *J. Chem. Phys.*, **78**, 6338 (1983).
- "Research is Engineering", *Chem. Eng. Educ.*, 190 (Fall 1982).
- "On the Time Required to Reach Fully Developed Flow in Pulsed Supersonic Free Jets", with K. L. Saenger, *J. Chem. Phys.*, **79**, 6043 (1983).
- "Clustering in Free Jets—Aggregation by Dispersion", with S. B. Ryali, *Ber. Bunsenges. Phys. Chem.*, **88**, 245 (1984).
- "The Electropray Ion Source—Another Variation on the Free Jet Theme", with Masamichi Yamashita, *J. Phys. Chem.*, this issue.

#### Books

- "Engines, Energy and Entropy—A Thermodynamics Primer", W. H. Freeman, San Francisco, 1982.

## Electropray Ion Source. Another Variation on the Free-Jet Theme

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Solutions passed through a small capillary at 2–10 kV relative to ground are electrosprayed into a bath gas to form a gaseous dispersion of ions that is expanded into vacuum in a small supersonic free jet. A portion of the jet is passed through a skimmer to form a molecular beam that contains a variety of ionic species. Mass spectrometric analysis reveals that these species include solute cations in aggregation with solvent molecules and/or nonionized solute species. The nature of the product ions depends upon the composition and feed rate of the original solution, the temperature and composition of the bath gas, and the voltage applied to the capillary. The exploratory experiments reported here suggest that this novel ion source may be useful for producing in vacuo a wide variety of cluster ions for examination by various spectroscopic techniques. Also inviting is the prospect of extending the applicability of mass spectrometric analysis to large organic molecules that are too complex, too fragile, or too nonvolatile for ionization by more conventional methods. Another intriguing possibility is to use the technique on probing the microscopic structure and properties of solutions.

### Introduction

Beginning about 15 years ago Malcolm Dole and his colleagues carried out a provocative series of ingenious experiments in which they attempted to generate in vacuo beams of macromolecules, more properly macroions.<sup>1-5</sup> Their approach was to electropray a dilute solution of polystyrene molecules into a bath gas of nitrogen at atmospheric pressure. The idea was that as the solvent (3:2 benzene:acetone) evaporated from the charged droplets the charge density on the surface would increase until the Rayleigh limit was reached at which the Coulomb repulsion forces begin to exceed the surface tension and the droplet would subdivide. If this division process continued far enough and if the original solution were dilute enough a state would be reached in which an average each droplet would contain only one macromolecule. After the remaining solvent evaporated at least some of the charge should remain on the macromolecule. The net result would be a dispersion of macroions in the bath gas which could be expanded

through a small supersonic jet into a vacuum chamber in what has become the commonplace method for producing molecular beams having high intensities and narrow velocity distributions.

The effectiveness of this very clever idea was demonstrated by Dole and his colleagues in two sets of experiments carried out in two separate laboratories using two somewhat different apparatus designs. With polystyrene molecules ranging in mass from 200 to 860 000 daltons they obtained ion currents from 10<sup>-14</sup> to nearly 6 × 10<sup>-13</sup>A. By assuming that the macroions reached the terminal gas velocity in the free jet they obtained some values for mass/charge ratios that correspond to what would be expected

(1) M. Dole, L. L. Mack, R. L. Hines, R. C. Mobley, L. D. Ferguson, and M. B. Alice, *J. Chem. Phys.*, **49**, 2240 (1968).

(2) L. L. Mack, P. Kralik, A. Rheude, and M. Dole, *J. Chem. Phys.*, **52**, 4977 (1970).

(3) G. A. Clegg and M. Dole, *Biopolymers*, **10**, 821 (1971).

(4) D. Teer and M. Dole, *J. Polym. Sci.*, **13**, 985 (1975).

(5) M. Dole, H. L. Cox, Jr., and J. Gieniec, *Adv. Chem. Ser.*, No. **125**, 73 (1973).

<sup>†</sup> On leave from the Institute of Space and Astronautical Science, Tokyo.

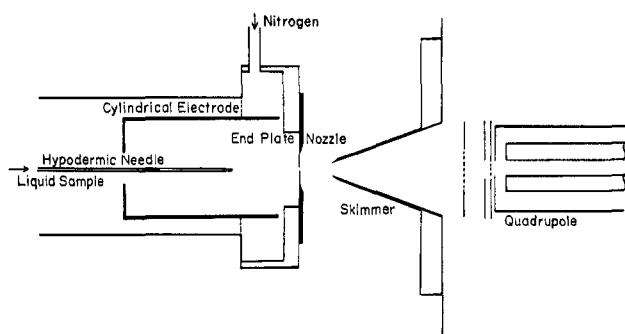


Figure 1. Schematic diagram of electrospray ion source.

for singly charged macromolecules. Intrigued with these results we assembled an apparatus similar to Dole's and obtained results that were essentially equivalent. However, we were unable to solve two severe experimental problems. In the first place, the retarding potential method of estimating mass/charge was not very satisfactory and there seemed to be no readily available alternatives for determining masses of very large ions. In the second place, these large macroions did not give rise to any secondary electrons when they struck the first dynode of an electron multiplier. Thus, we were denied the gains of  $10^5$  or  $10^6$  that multipliers can provide and that would have made the detection problem much less refractory. To be sure, Beuhler and Friedman have shown that large ions will give secondary electrons if they have a high enough energy.<sup>6</sup> Unfortunately, the 500-kV acceleration that they found necessary for some large cluster ions is not an attractive option in most laboratories, certainly not in ours. Consequently, we abandoned further work on macroion beams. Dole also stopped publishing on this subject, perhaps for the same reason.

About three years ago we became concerned with the problem of putting some complex and relatively nonvolatile molecules into the gas phase without decomposition so that we could expand them in free jets for infrared spectroscopic studies. This concern rekindled our interest in Dole's electrospray process so we started an investigation aimed at understanding the details of the electrospray-droplet evaporation sequence in the hope that we might learn how to obtain solute ion currents large enough for spectrometric examination. Instead of macromolecules we planned to use solute species with molecular weights small enough so that we could mass analyze the ions with an available quadrupole mass filter that had a maximum mass range of about 450 daltons. By such analysis we hoped to elucidate the fairly complex sequence of processes by which charged droplets divide as they evaporate. The dependence of final ion mass distribution upon spray parameters such as solution composition, feed rate, and applied voltage should help characterize the path that leads from original feed liquid to final free-jet ion. We also hoped that this path might represent a route by which solute species smaller than macromolecules, but still not volatile enough to vaporize without decomposition, might become ions in vacuo ready for mass analysis. The intense and growing demand for interface between a mass spectrometer and a liquid chromatograph has motivated a vigorous search for such a route. This communication comprises our first report on the interesting and to-us-somewhat-unexpected results that we have obtained in our early studies.

### Experimental Apparatus and Procedures

Figure 1 is a schematic representation of the essential features of the apparatus. Liquid sample was introduced through a stainless steel hypodermic needle (B&S gauge 26s with an i.d. of 0.1 mm) chamfered at the end to form a sharp edged conical tip and maintained at 3–10 kV relative to ground. The distance from the end of the needle to an end plate containing the nozzle was in the range from 20 to 30 mm. Surrounding this region was a cylindrical electrode 30 mm in diameter and maintained at 500–600 V relative

to ground. Dry nitrogen typically at 1050 torr was passed through the region at a velocity of several cm/s in order to sweep out solvent vapor from the evaporating droplets. The nozzle comprised a 70- $\mu$ m hole photochemically etched in stainless steel shim stock 0.1 mm thick (Toppan Co., Tokyo). A platinum electron microscope aperture of similar diameter (Ladd Research, Vermont) was also used as a nozzle. The region downstream of the nozzle was maintained at a few mtorr or less by an oil diffusion pump with a speed of 1000 L/s. A portion of the resulting free jet was passed through a skimmer with a 4-mm aperture into a vacuum chamber containing the quadrupole mass filter and pumped by a pair of baffled 6-in. oil diffusion pumps with a combined speed of the order of 3000 L/s. The quadrupole comprised an EAI probe (QAD 250 RGA) with an Extranuclear power supply (QPS 111) and was fitted with a ceramic channeltron detector (Murata Mfg., Kyoto). An electron bombardment ion source was also in place for the purpose of calibrating the spectrometer with respect to mass number. Voltages applied respectively to the end plate (nozzle), skimmer, and ion lens of the analyzer were typically +40, +10, and -100 V relative to ground. No other focusing of ions was attempted. The total current to the end plate, essentially the total electrospray current, was monitored.

Solution samples were made up with deionized water distilled in a quartz apparatus. All other solvents and solutes were taken as received from the supplier and were usually analytical grade. Nitrogen bath gas was supplied from vaporizing liquid. At rates below 0.1  $\mu$ L/s the solution was fed from a pressurized reservoir through a long capillary to the hypodermic needle. At higher rates (up to a few  $\mu$ L/s) the solution was fed by a positive displacement syringe pump driven by a powered lead screw. Because of the voltages applied to the needle both of these solution sample sources had to float with respect to ground.

### Results and Discussion

**General Behavior of the Electrospray.** The electrospray process had been studied by a number of investigators in connection with applications ranging from painting and printing to the generation of charged colloids for use as propellants in so-called ion rockets.<sup>7–19</sup> We will make no attempt to review and summarize these studies but will only present a simple phenomenological working description of the process based on our own observations made in some preliminary experiments in the "open air" of the laboratory supplemented by what we have been able to infer from results obtained with the apparatus described in the preceding section. It is useful to bear in mind that most of the behavior that we describe depends upon the competition between Coulomb forces due to charge with droplet surface and the tension of that surface due to attraction between the liquid molecules.

When the solution flow is started in the absence of any applied voltage liquid drops form at the end of the capillary. They detach and fall when they become large enough so that the gravitational force due to their mass exceeds the surface tension forces that attach them to the liquid column in the capillary (and the latter's end surfaces). If a voltage is applied to the capillary the first visible effect is that the trajectories of the falling droplets begin to have a horizontal component in the direction of the end plate. As the potential difference between the capillary and the end plate in-

(7) V. G. Drozin, *J. Colloid Sci.*, **10**, 158 (1955).

(8) C. D. Hendricks, Jr., R. S. Carson, J. J. Hogan, and J. M. Schneider, *AIAA J.*, **2**, 733 (1964).

(9) J. J. Hogan and C. D. Hendricks, *AIAA J.*, **3**, 296 (1965).

(10) S. A. Ryce and D. A. Patriarche, *Can. J. Phys.*, **43**, 2192 (1965).

(11) R. J. Pfeifer and C. D. Hendricks, *Phys. Fluids*, **10**, 2149 (1967).

(12) D. Michelson, *J. Fluid Mech.*, **33**, 573 (1968).

(13) W. E. DeShon and R. S. Carson, *J. Colloid Interface Sci.*, **28**, 161 (1968).

(14) J. D. Shorey and D. Michelson, *Nucl. Instrum. Methods*, **82**, 295 (1970).

(15) M. N. Huberman, *J. Appl. Phys.*, **41**, 578 (1970).

(16) S. B. Sample and R. Bollini, *J. Colloid Interface Sci.*, **41**, 185 (1972).

(17) R. Bollini and S. B. Sample, *Colloid Interface Sci.*, **3**, 291 (1976).

(18) A. J. Kelly, *J. Appl. Phys.*, **47**, 5264 (1976).

(19) A. J. Kelly, *J. Appl. Phys.*, **49**, 2621 (1978).

(6) R. J. Beuhler and L. Friedman, *Nucl. Instrum. Methods*, **170**, 309 (1980).

TABLE I

liquid sample	low-voltage mode ions	high-voltage mode ions
H <sub>2</sub> O		(H <sub>2</sub> O) <sub>m</sub> ·H <sup>+</sup> , (H <sub>2</sub> O) <sub>n</sub> <sup>+</sup>
CH <sub>3</sub> OH	(CH <sub>3</sub> OH) <sub>m</sub> ·(H <sub>2</sub> O) <sub>n</sub> ·Na <sup>+</sup> ( <i>m</i> = 0, 1), (CH <sub>3</sub> OH) <sub>m</sub> ·H <sup>+</sup> , (CH <sub>3</sub> OH) <sub>m</sub> ·H <sub>2</sub> O <sup>+</sup>	(CH <sub>3</sub> OH) <sub>m</sub> ·H <sup>+</sup> , (CH <sub>3</sub> OH) <sub>m</sub> ·H <sub>2</sub> O <sup>+</sup> , (CH <sub>3</sub> OH) <sub>m</sub> ·C <sub>2</sub> H <sub>6</sub> <sup>+</sup>
C <sub>2</sub> H <sub>5</sub> OH-LiCl ( <i>x</i> = 4.3 × 10 <sup>-5</sup> )	(C <sub>2</sub> H <sub>5</sub> OH) <sub>m</sub> ·Li <sup>+</sup>	(C <sub>2</sub> H <sub>5</sub> OH) <sub>m</sub> ·H <sup>+</sup> , (C <sub>2</sub> H <sub>5</sub> OH) <sub>m</sub> ·H <sub>2</sub> O <sup>+</sup> , (C <sub>2</sub> H <sub>5</sub> OH) <sub>m</sub> ·C <sub>3</sub> H <sub>8</sub> <sup>+</sup>
CH <sub>3</sub> COCH <sub>3</sub> -LiCl ( <i>x</i> = 1.0 × 10 <sup>-4</sup> )	(CH <sub>3</sub> COCH <sub>3</sub> ) <sub>m</sub> ·Li <sup>+</sup>	(CH <sub>3</sub> COCH <sub>3</sub> ) <sub>m</sub> ·(H <sub>2</sub> O) <sub>n</sub> ·H <sup>+</sup> ( <i>m</i> = 0.1), (CH <sub>3</sub> COCH <sub>3</sub> ) <sub>m</sub> ·C <sub>2</sub> H <sub>6</sub> <sup>+</sup> , (CH <sub>3</sub> COCH <sub>3</sub> ) <sub>m</sub> ·C <sub>3</sub> H <sub>8</sub> <sup>+</sup>
CH <sub>3</sub> CN	(CH <sub>3</sub> CN) <sub>m</sub> ·Na <sup>+</sup>	(CH <sub>3</sub> CN) <sub>m</sub> ·C <sub>2</sub> H <sub>6</sub> <sup>+</sup> , (CH <sub>3</sub> CN) <sub>m</sub> ·C <sub>3</sub> H <sub>8</sub> <sup>+</sup> , (CH <sub>3</sub> CN) <sub>m</sub> ·H <sub>2</sub> O <sup>+</sup>
CH <sub>3</sub> OH + H <sub>2</sub> O (50:50)	(CH <sub>3</sub> OH) <sub>m</sub> ·(H <sub>2</sub> O) <sub>n</sub> ·Na <sup>+</sup>	(CH <sub>3</sub> OH) <sub>m</sub> ·H <sup>+</sup> , (CH <sub>3</sub> OH) <sub>m</sub> ·H <sub>2</sub> O <sup>+</sup> , (CH <sub>3</sub> OH) <sub>m</sub> ·C <sub>2</sub> H <sub>6</sub> <sup>+</sup>
CH <sub>3</sub> OH + H <sub>2</sub> O (50:50); HCl ( <i>x</i> ~ 10 <sup>-4</sup> ); LiCl ( <i>x</i> = 6.7 × 10 <sup>-5</sup> ); NaCl ( <i>x</i> = 9.5 × 10 <sup>-5</sup> ) (CH <sub>3</sub> ) <sub>4</sub> Ni ( <i>x</i> = 9.2 × 10 <sup>-6</sup> )	(CH <sub>3</sub> OH) <sub>m</sub> ·(H <sub>2</sub> O) <sub>n</sub> ·X <sup>+</sup> , X = H, Li, and Na  (CH <sub>3</sub> OH) <sub>m</sub> ·(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup>	(CH <sub>3</sub> OH) <sub>m</sub> ·H <sup>+</sup> , (CH <sub>3</sub> OH) <sub>m</sub> ·H <sub>2</sub> O <sup>+</sup> , (CH <sub>3</sub> OH) <sub>m</sub> ·C <sub>2</sub> H <sub>6</sub> <sup>+</sup>

creates the detaching droplet become smaller and their horizontal components become greater. If the liquid flow rate remains constant the drops increase their detachment frequency as they decrease their size. In addition, their speed increases. As the applied voltage continues to rise the droplets become visibly elongated in the direction of the end plate while they are attached to the capillary and their trajectories approach a nearly horizontal trajectory toward the end plate. Under these conditions close examination reveals that the droplets are forming at the end of a column of liquid that extends beyond the end of the capillary. Further increases in voltage result in the elongation of this column and a narrowing of its tip to a fairly sharp point. At this juncture the departing droplets have become so small that they are barely in the Tyndall effect sense for a very short distance from the end of the liquid column before they become "completely" evaporated. As the voltage is still further increased there is a sudden transition to a condition in which a fine mist of droplets is produced from a number of source points scattered around the sharp edge of the capillary tip and the central liquid column vanishes. The potential at which this transition takes place depends somewhat on the liquid composition, the shape and finish of the capillary tip, probably the pressure and composition of the ambient gas, but mostly on the distance between the tip and the endplate, i.e., the local field strength. We will refer to behavior at voltages below and above the transition value as the "low-voltage mode" and the "high-voltage mode".

It is interesting to note what happens to the current carried by the charged droplets and their derivative vapor ions to the end plate containing the nozzle aperture. This current,  $I_t$ , representing essentially the total current dissipated in the electrospray, depends on the needle voltage,  $V_n$ , and the distance between the needle and the end plate. Figure 2 shows the dependence of  $I_t$  on  $V_n$ . The slope is fairly small in the low-voltage mode but rises steeply with some oscillation as the high-voltage mode is reached. Addition of electrolyte to the liquid increases the current in the low-voltage mode but does not effect the high-voltage current appreciably. Clearly, somewhat different processes or mechanisms must be involved in these two different modes. Mass analysis of the free-jet ions provides some information on these differences and will be considered later. Meanwhile, it is important to remember that in their journey from the end of the capillary to the end plate the original droplets and their derivative ions are drifting through the nitrogen bath gas, undergoing many collisions with the bath gas molecules, and arriving at some state of solvation determined by the transit time, the bath gas temperature, and the effective concentration of solvent vapor in the bath gas. From estimates of the field strength and the ion mobilities we arrive at a rough figure for the transit time of the order of 10 ms. Only thermodynamically stable ions will survive this treatment. Moreover, after so many collisions they are almost sure to be in the ground state with respect to internal energy.

**Mass Analysis of Free-Jet Ions During Low-Voltage Electrospraying of Solvents Containing Relatively Simple Solute Cations.** As the ionic products of the electrospray approach the end plate a small fraction becomes entrained in the bath gas that

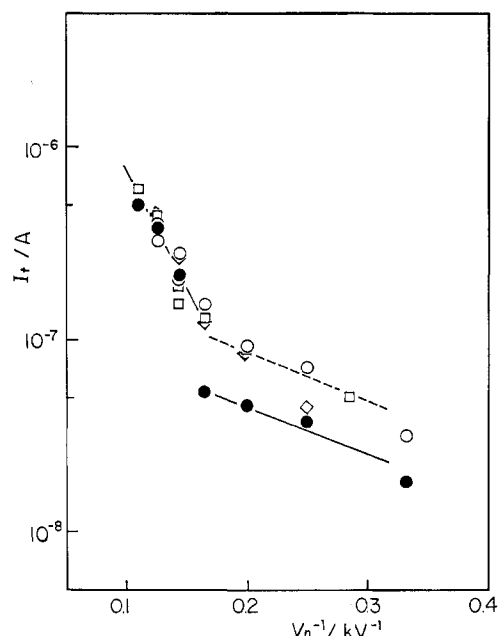


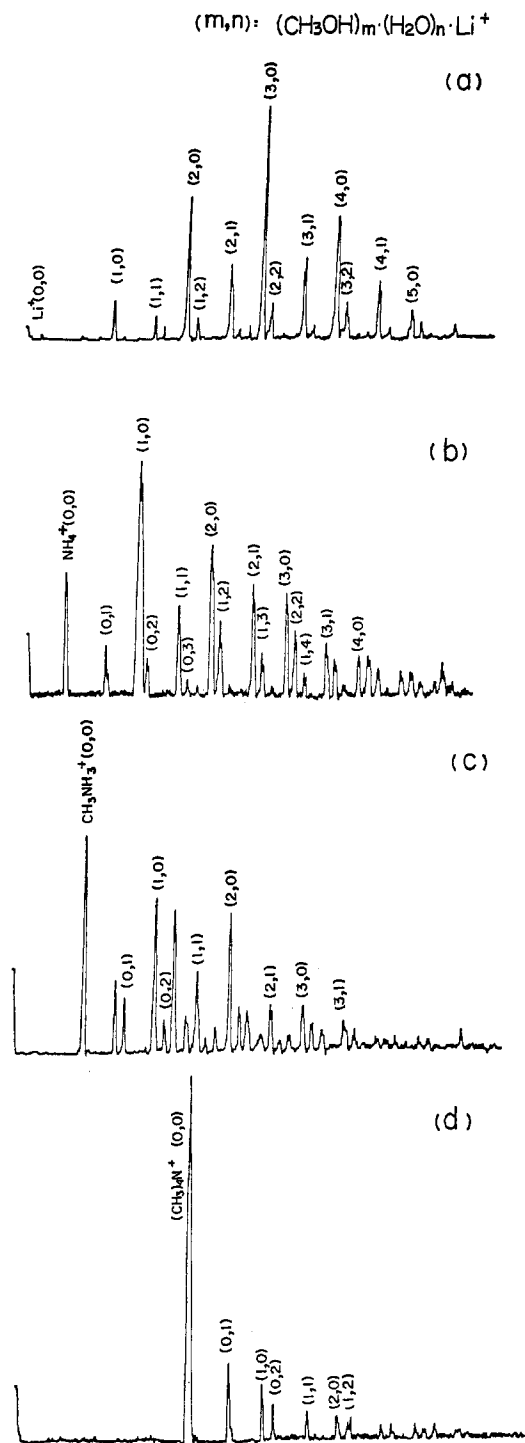
Figure 2. Dependence of total electrospray ion current on voltage applied to capillary: 50-50 methanol-water mixture with HCl (*x* = 10<sup>-4</sup>), with LiCl (*x* = 6.7 × 10<sup>-5</sup>), with NaCl (*x* = 9.5 × 10<sup>-5</sup>).

flows into the nozzle aperture to form the free jet. A fraction of the ions emerging in the jet passes through the skimmer and is analyzed in the quadrupole. It is important that jet gas be as free as solvent vapor as possible. Otherwise the low temperatures reached during the adiabatic expansion will cause condensation of the vapor on the ions to form clusters that can become very large.<sup>20,21</sup> The reality of this effect is indicated by the fact that if the liquid feed rate is increased or if the bath gas flow is decreased, other conditions remaining the same, the ion currents for all the mass peaks (within the mass range of the quadrupole) drop sharply even though the total spray current to the end plate remains the same. Moreover, the smaller cluster ion populations decrease more than the larger ones.

Table I identifies the ion species found for various solvent-solute combination in both the low-voltage and high-voltage modes of operation. Let us turn our attention first to the low-voltage results. Pure water gave no appreciable ion currents at any mass within the range of the quadrupole. It seems likely that its relatively low vapor pressure and relatively high heat of vaporization conspire to give evaporation rates so low that the cluster ions arriving at the nozzle inlet are too massive to be detected, especially if there is residual water vapor in the bath gas that would let clusters grow during the expansion. For this reason most of our subsequent results were obtained with more volatile solvents. A 50-50 mixture

(20) J. Q. Searcy and J. B. Fenn, *J. Chem. Phys.*, **61**, 5282 (1974).

(21) J. Q. Searcy, *J. Chem. Phys.*, **63**, 4114 (1975).



**Figure 3.** Mass spectrum of cluster ions for an electrospray of 50–50 methanol–water solutions in the low-voltage mode: (a) LiCl ( $x = 6.7 \times 10^{-3}$ ); (b)  $(\text{NH}_4)_2\text{CO}_3$ ; (c)  $\text{CH}_3\text{NH}_2$  ( $x = 7.0 \times 10^{-4}$ ); (d)  $(\text{CH}_3)_4\text{NI}$  ( $x = 9.2 \times 10^{-6}$ ).

of methanol and water was used in many experiments because it combines volatility with an ability to dissolve a wide range of interesting solutes. As shown in the table this solvent by itself gives rise to protonated solvent clusters along with some ions comprising solvent molecules in aggregation with contaminant sodium cations. Deliberate addition of electrolytes results in the formation of cluster ions comprising the added cation combination with varying numbers of solvent molecules. It also increases the total current to the end plate as mentioned earlier. Figure 3 shows the distribution of cluster ion masses obtained with the following solutes in the methanol–water solvent: LiCl,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{CH}_3\text{NH}_2$ , and  $(\text{CH}_3)_4\text{NI}$ . In the order given the number of solvent molecules in association with each cation decreases. Low-voltage

results with the other solvents are similar to the cases mentioned and require no further comment.

There are two important conclusions to be drawn from these low-voltage data. The first is that the ionization is very gentle in that there is no evidence of any fragmentation or decomposition of either solvent or solute species. Except for “concentration” the ratio of solvent to solute species there seems to be a nearly one-to-one correspondence between the liquid phase and the gas phase. Only those molecular species in the solution are found in the gas-phase ions. The only differences are in the degree of aggregation. The second important conclusion requires a bit of arithmetic. The solute ions, for example  $\text{Li}^+$ , always appear singly in any of the clusters. The importance of this observation emerges from a comparison of the total ion current in the spray with the total flux of lithium in the solution feed. A typical combination is  $1 \mu\text{L/s}$  of 50–50 methanol–water containing LiCl with a mole fraction  $x = 6.7 \times 10^{-5}$ . The electric current corresponds to about  $1.3 \times 10^{12}$  elementary charges/s. The mass flux corresponds to about  $1.7 \times 10^{15}$   $\text{Li}^+\text{Cl}^-$  ion pairs/s. Thus, there are about 1000 of these ion pairs for each positive charge (missing electron) in the electrospray electric current. Question: How does a single  $\text{Li}^+$  escape this multitude of peers and emerge with an entourage of solvent molecules as a gas-phase cluster ion. The sequence invoked by Dole, successive charged droplet subdivisions with interludes of evaporation that increase surface charge density to power the next subdivision, clearly cannot apply. For the case under consideration the last possible step in such a sequence would result in a droplet with a single excess charge containing a 1000  $\text{Li}^+\text{Cl}^-$  solute ion pairs. And yet, the mass spectrometer tells us that solvated individual Li ions appear in substantial numbers.

The question had in fact been already answered before we knew enough to ask it. Iribarne and Thomson in a very perceptive paper had concluded that the field intensity at the surface of a charged evaporating droplet could become high enough to desorb a solute ion from the droplet liquid.<sup>22</sup> Moreover, in support of their model, they offered experimental evidence obtained from mobility measurements of both positive and negative ions in a mist of charged droplets produced by atomizing solutions with various solute species. In a subsequent paper, they presented mass spectrometric analyses of the desorbed ions.<sup>23</sup> In many ways the results obtained with their atmospheric pressure ion vaporization (APIE) source are quite similar to ours and certainly were earlier. However, there are significant differences between the two studies and because the ion desorption phenomena appears to have many practical implications and applications, we thought it worthwhile to communicate our findings even if they served only to confirm the Iribarne–Thomson hypothesis. The major differences relate mostly to the method of producing charged droplets. Iribarne and Thomson achieved droplet charging by the spraying process itself. Random fluctuations in the division of charge between droplets are obtained when a small stream of solution containing an ionized solute is atomized by a transverse flow of high-velocity gas. The net charge on the droplets is substantially enhanced by the presence of an induction electrode that polarizes the charge distribution in the liquid while it is being atomized. The resulting spray or mist contains both positively and negatively charged droplets and is overall approximately neutral.

Whereas Iribarne and Thomson bring about charging by atomization, we bring about atomization by charging. By applying a high voltage to the stream of source liquid we achieve a high charge density on the liquid surface. The consequent Coulomb forces overcome surface tension and bring about atomization. The net result is a dispersion of droplets with like charge instead of a mixture of droplets having opposite charges. Because the charging voltage is easily varied we have a more direct control of the charging-atomization process. Moreover, because the

(22) J. V. Iribarne and B. A. Thomson, *J. Chem. Phys.*, **64**, 2287 (1976).

(23) B. A. Thomson and J. V. Iribarne, *J. Chem. Phys.*, **71**, 4451 (1979); J. V. Iribarne, P. J. Dziedzic, and B. A. Thomson, *Int. J. Mass Spectrom. Ion Phys.*, **50**, 331 (1983).

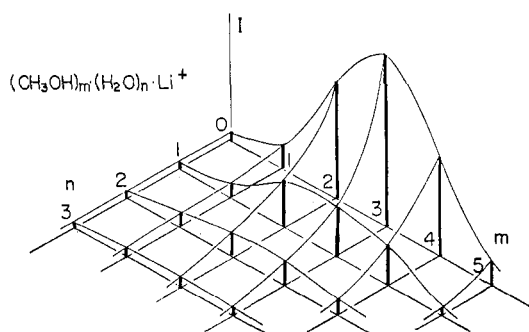


Figure 4. Three-dimensional representation of the distribution of cluster ions from the spectrum shown in Figure 3a.

current flow in the spray is easily monitored our bookkeeping on the charge flux and distribution is a bit more accurate than can be the case with the atomizer-induction electrode combination. Indeed it is this bookkeeping feature that forced us to question and discard the Dole model. It provides the best yet confirmation of the Iribarne-Thomson mechanism for the production of gas-phase ions containing only one solute ion or molecule. It is also not surprising that the electrospray approach seems to provide substantially higher ion currents into the spectrometer than can be obtained by atomizer-induction electrode combination.

Also relevant to these considerations are the interesting experiments of the group comprising Stimpson, Simons, Evans and Colby, who electrosprayed glycerol solutions of various fragile molecules directly into a vacuum chamber containing a mass spectrometer.<sup>24-26</sup> They also found that solute ions were apparently directly desorbed from the solution surface by the high field achieved. Our approach is in one sense very similar to theirs. However, by electrospraying into a bath gas instead of a vacuum, we are not constrained to the use of very nonvolatile solvents such as glycerol. In addition, we can more readily control the energy of the ions entering the mass analyzer because the bath gas prevents the high fields required for electrospray dispersion from accelerating the ions to correspondingly high energies. Another advantage of the bath gas buffer is that it avoids fouling of the high-vacuum portion of the apparatus with nonvolatile solvent material.

Although the Iribarne-Thomson model almost surely embodies the most reasonable explanation for the presence of the ions the mass spectrometer identifies, much remains to be learned about the desorption process before we can claim to understand it thoroughly. Moreover, it will be difficult to acquire the kind of information that is needed. For example, it is most important to know the exact composition of the ion clusters as they leave the surface of the liquid. Unfortunately on their way to the spectrometer, they must inevitably traverse an ill-defined path involving evaporation conditions upstream of the nozzle and condensation conditions in the free-jet expansion. It is most likely that educated guesses as to the original ion composition will be possible only after a large amount of data has been obtained over a wide range of the pertinent variables including solution composition, applied voltage, bath gas temperature, pressure and composition, and nozzle diameter, to name the obvious ones. All we can do at this stage in our studies is to present some representative data that are illustrative of what we have observed and indicative of some of the kinds of trends that can be expected.

Figure 4 comprises a three-dimensional representation of the cluster composition reflected in the Figure 3a, the low-voltage electrospray spectrum for LiCl in methanol water. There is a clear bias toward methanol in the mixed clusters similar to that found in the case of proton clusters reported by Kebarle.<sup>42</sup> He attributes this propensity to the higher polarizability of the CH<sub>3</sub> group

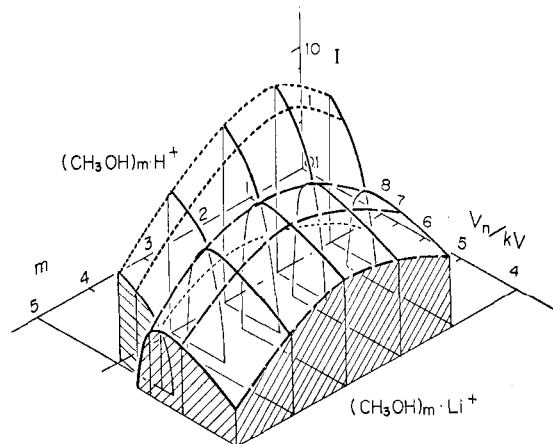


Figure 5. Three-dimensional representation of the voltage dependence of several cluster ion species in spectra equivalent to Figure 3a.

relative to H and characterizes it in terms of a preference factor  $\gamma_n$ . It is defined as the molecular ratio of CH<sub>3</sub>OH to H<sub>2</sub>O in a cluster of  $n$  molecules to the same ratio in the gas phase. For H<sub>+</sub> the value of  $\gamma_n$  decreases from about 200 when  $n$  is 3 to 25 when  $n$  is 6. Over that same range of  $n$  our Li<sup>+</sup> data show  $\gamma_n$  decreasing from about 20 to 6. Too much should not be made of the relative absolute values of this preference factor because Kebarle's data purports to represent equilibrium between cluster and vapor. We cannot pretend to have achieved equilibrium in our experiment. The roughly parallel behavior does suggest that our cluster compositions may be determined much more by gas-phase processes than by what happens before the ion desorbs.

The voltage applied to the needle is an easily controlled variable and it is appropriate to examine its effect. Figure 5 shows the voltage dependence of ion currents for cluster ions of Li<sup>+</sup> and H<sup>+</sup> solvated only with methanol in the electrospray spectrum for the solution of LiCl in methanol-water mentioned above. Note that applied voltage increases toward the origin. In the low-voltage regime all the ions have a Li<sup>+</sup> core. The current increases gradually for each species to a maximum value. Beyond this maximum further increases in applied voltage result in a sudden catastrophic decrease in Li<sup>+</sup> cluster ion currents accompanied by the appearance of and sharp rise in H<sup>+</sup> cluster ion currents. This abrupt change occurs at the transition from the low-voltage to the high-voltage mode that we described earlier in terms of the visible changes in spray pattern. It is now time to return our attention to this high-voltage behavior.

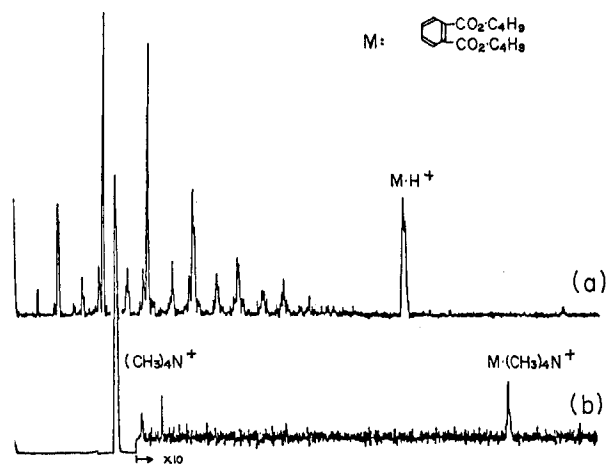
**Mass Analysis of Free-Jet Ions in the High-Voltage Mode.** The abrupt change in ion composition that we described at the end of the last section happens with all solutions that we have tried. The sudden switch from Li<sup>+</sup> to H<sup>+</sup> as the core ion is not easy to understand in terms of the field-ion desorption mechanism of Iribarne and Thomson. Nor is it obvious just what other process could bring about this change. Inspection of Table I provides some clues. It reveals that the observed ions include not only species that one presumes are in the liquid phase but also species which could only result from fragmentation or decomposition reactions. Consider the case of LiCl in acetone, for example. In the low-voltage mode only Li<sup>+</sup>-acetone clusters are seen. In the high-voltage mode these species disappear and we find some H<sup>+</sup>-acetone cluster, alone and with ethane, propane, and water adducts. We confirmed the identity of the ethane and propane adducts by adding D<sub>2</sub>O to the acetone. It turns out that all of the acetone hydrogens exchange with deuterium from the heavy water. Thus, the changes in peak masses when D<sub>2</sub>O is added show the number of hydrogens in the molecule and provide fairly persuasive evidence for the identity of these adducts. It is interesting to note that in the case of methanol only the H attached to the O exchanges with D.

It is also to be noted that the mass 18 ion that we have observed has two possible identities: H<sub>2</sub>O<sup>+</sup> or NH<sub>4</sub><sup>+</sup>. Because its intensity depends very strongly on the concentration of water in the original solution we are inclined to believe that at least most of this peak

(24) D. S. Simons, B. N. Colby, and C. A. Evans, Jr., *Int. J. Mass Spectrom. Ion Phys.*, **15**, 291 (1974).

(25) B. P. Stimpson and C. A. Evans, Jr., *Biomed. Mass Spectrom.*, **5**, 52 (1978).

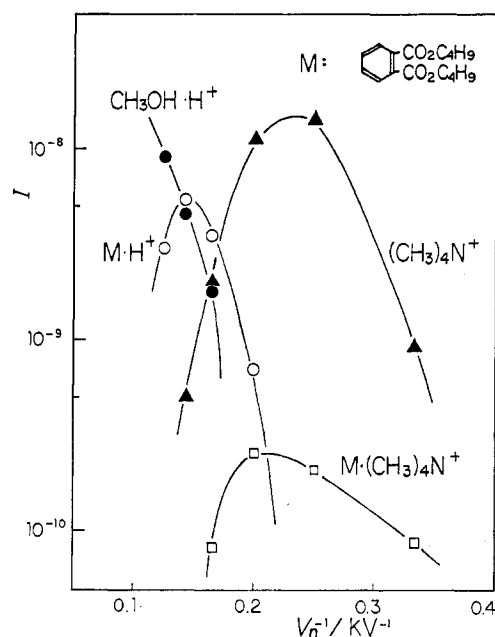
(26) B. P. Stimpson, D. S. Simons, and C. A. Evans, Jr., *J. Phys. Chem.*, **82**, 660 (1978).



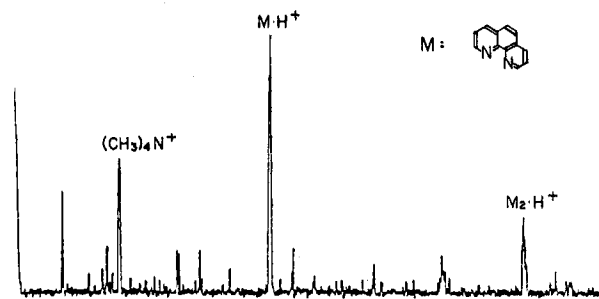
**Figure 6.** Mass spectrum of *n*-dibutyl phthalate ( $x = 1.3 \times 10^{-5}$ ) and  $(\text{CH}_3)_4\text{NI}$  ( $x = 7.6 \times 10^{-7}$ ) in 50–50 methanol–water. Capillary voltage: (a) +7 kV; (b) +4 kV.

does correspond to  $\text{H}_2\text{O}^+$  as proposed by Tsuchiya et al.<sup>27</sup> Other core ion masses have several possible identities:  $\text{NO}^+$ ,  $\text{CH}_2\text{O}^+$ , and  $\text{C}_2\text{H}_6^+$  for mass 30;  $\text{N}_2\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{C}_2\text{H}_4\text{O}^+$ , and  $\text{C}_3\text{H}_8^+$  for mass 44 and so on. In view of all the “foreign” mass peak possibilities that emerge when the electrospray is operating in the high-voltage mode, it seems obvious that some kind of chemical reaction is occurring. Two possibilities suggest themselves. One is that the high fields at the droplet surface bring about these chemical changes in the surface layer or during the desorption. The other is that the applied voltage has become high enough to bring about partial breakdown and a Townsend or glow discharge in the gas phase. The fact that an abrupt increase in total current is associated with the onset of the high voltage makes us favor the latter explanation. Although in one sense the high-voltage mass spectra are much messier than those obtained in the low-voltage mode, the difference between them could turn out to be useful. As an ion source for mass spectrometry of fragile molecules, an application that we think is most promising and which we will discuss in the next section, these two modes could well supplement each other. The low-voltage mode would provide information on parent molecule molecular weight. The fragments obtained in the high-voltage mode could help determine the chemical identity of that parent molecule.

**Mass Analysis of Free-Jet Ions When Complex Solute Species Are Present.** All the mass spectra we have considered thus far were obtained with fairly simple electrolytes as solutes. The most intriguing aspect of electrospray ion formation is what happens when more complex molecules are used as a solute species. Figure 6 shows the spectrum obtained when *n*-dibutyl phthalate is present at a mole fraction of  $1.3 \times 10^{-5}$  in 50–50 methanol–water along with a trace of tetramethylammonium iodide ( $x = 7.6 \times 10^{-7}$ ). The remarkable feature of this spectrum is that this large nonpolar molecule attaches itself to a cation and desorbs from the solution with no solvent molecules in tow. At least there are no solvent molecules present by the time it gets to the mass spectrometer. There is no evidence of fragmentation of the dibutyl phthalate, but we can say nothing about the possible appearance of dimer ions of this solute because their mass is outside the range of the spectrometer. Figure 7 shows the voltage dependence of ion currents in this spectrum. The behavior is very similar to the case of solvent cluster ions in Figure 5. As the voltage increases the ion current corresponding to dibutyl phthalate attached to an  $\text{N}(\text{CH}_3)_4^+$  increases until a maximum is reached and then decreases sharply. At this point a phthalated  $\text{H}^+$  ion current begins a rapid rise and achieves a higher maximum current at a higher voltage before finally dropping off. Meanwhile, the bare  $\text{N}(\text{CH}_3)_4^+$  ion current at somewhat higher levels parallels the behavior of its complex with dibutyl phthalate as an adduct when



**Figure 7.** Dependence of solute and solvent ion currents on applied capillary voltage. Solution is *n*-dibutyl phthalate ( $x = 1.3 \times 10^{-5}$ ) and  $(\text{CH}_3)_4\text{NI}$  ( $x = 7.6 \times 10^{-7}$ ) in 50–50 methanol–water.



**Figure 8.** Mass spectrum of 1,10-phenanthroline ( $x = 2.7 \times 10^{-5}$ ) and  $(\text{CH}_3)_4\text{NI}$  ( $x = 6.5 \times 10^{-8}$ ) in 50–50 methanol–water. Capillary voltage: +6 kV.

$\text{LiCl}$  is the source of solute ions similar behavior is observed with  $\text{Li}^+$  replacing  $\text{N}(\text{CH}_3)_4^+$  as the core ion in the desorbed species. This bias toward  $\text{H}^+$  as the core ion at high voltages seems to be quite general in our results. It is akin to the unusual stability of hydrated proton cluster ions in electrical discharges.

Another fairly complex molecule that desorbs as an ion from dilute methanol solution is phenanthroline. Figure 8 shows the spectrum obtained in the high-voltage mode. The protonated molecule species is the dominant peak but we can also see a protonated dimer peak which is within the mass range of the quadrupole. Figure 9 shows the voltage dependence of the desorbed ion currents.

Figures 10 and 11 show the interesting case of arginine as a solute species. Both protonated arginine and its dimer are found in the low-voltage mode and disappear at high voltages. We found no evidence of clusters containing other cations in aggregation with arginine. It seems reasonable to conclude that arginine is already protonated while it is in solution. The fact that electrospray ionization can produce intact ions of arginine without any fragmentation is a very intriguing result. This substance is notoriously difficult to analyze by mass spectrometry because like most amino acids it cannot be vaporized without decomposition. Further evidence of the ability of the electrospray to provide intact ions for normally nonvolatile species is given in Figure 12, which shows the electrospray mass spectrum for a “cocktail” of very nonvolatile species including one quaternary phosphonium and six quaternary ammonium halides dissolved in a 50–50 methanol–water solution. The relative magnitudes of the peaks correspond roughly to the relative concentrations of the species in

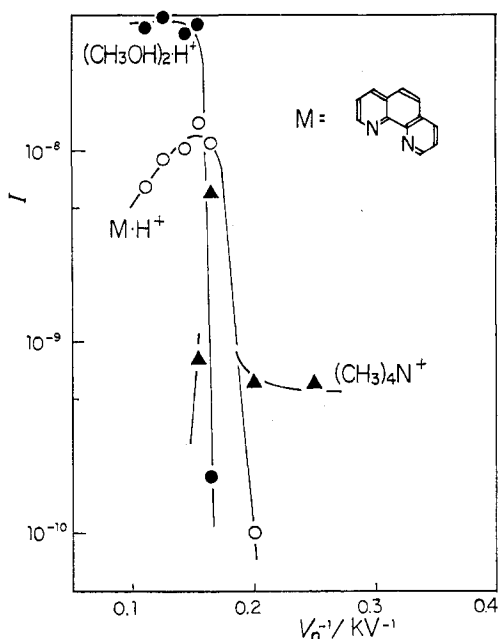


Figure 9. Dependence of ion currents on capillary voltage for solution of 1,10-phenanthroline ( $x = 2.7 \times 10^{-5}$ ) and  $(\text{CH}_3)_4\text{NI}$  ( $x = 6.5 \times 10^{-8}$ ) in 50-50 methanol-water.

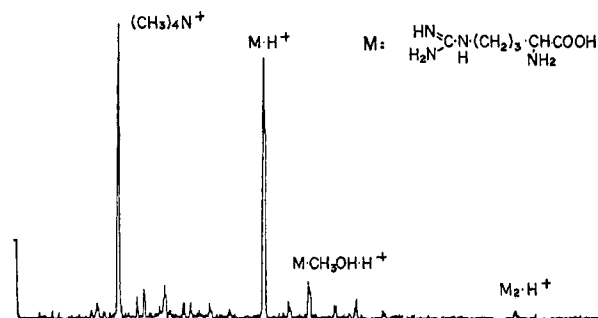


Figure 10. Electrospray mass spectrum for 22 ppm of arginine in 50-50 methanol-water solution containing 0.76 ppm of tetramethylammonium iodide.

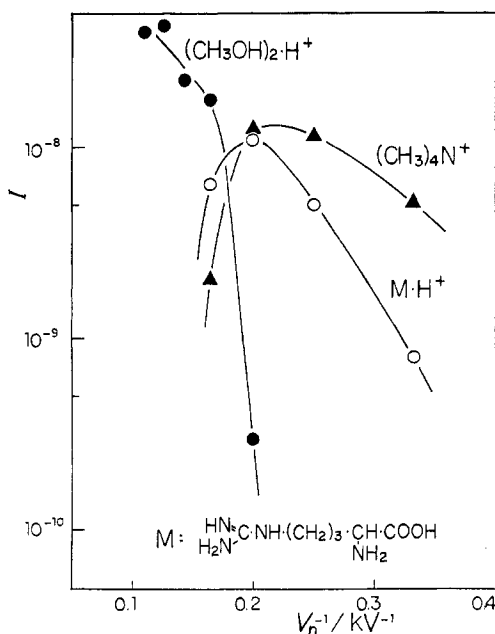


Figure 11. Dependence of ion currents on capillary voltage for spectrum shown in Figure 10.

the original solution but it is clear that calibration would be required before any quantitative analysis would be possible.

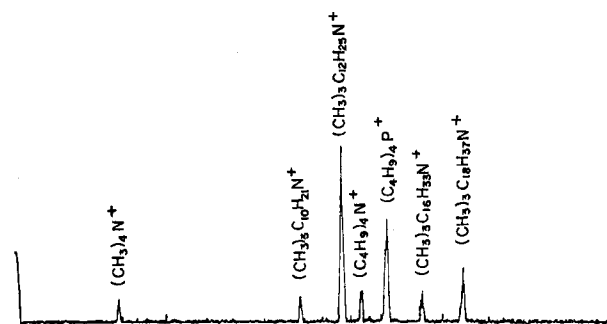


Figure 12. Electrospray mass spectrum for a mixture of quaternary ammonium and phosphonium halides in a 50-50 methanol-water solution.

It is also clear that for analytical purposes electrospray mass spectrometry seems to have the capability for high sensitivity. Although the concentrations of the solute species were only a few ppm the peaks are clearly discernible with a high signal-to-noise ratio. The spectrum was "taken" in a matter of 2 min on a chart recorder whose input was simply the output of the spectrometer multiplier. No signal averaging was involved. Moreover, the transmission efficiency for our quadrupole is only about  $10^{-3}$ ! Very provocative is the fact that the absence of fragmentation means that the parent species of the original solution are readily and unequivocally identified. With the kind of fragmentation encountered in conventional ion sources it would be extremely difficult to infer the original molecular composition of such a mixture from its mass spectrum.

These spectra that we have shown are only representative examples to illustrate the kind of results that can be obtained with what we are calling the electrospray ion source. We have obtained similar results with over 50 other solute species. Thomson and Iribarne similarly found that a wide range of solute species were desorbed as ions or as adducts to solute ions.<sup>23</sup> They also were able to detect desorbed anions with and without adduct molecules. After making the necessary modifications to our spectrometer, we too have obtained some results with negative ions from the electrospray source and will report on them when they are more complete.

It is noteworthy that Thomson and Iribarne were unable to obtain signals for divalent ions, either positive or negative. They attribute this failure to the much higher solvation energies to be expected with each species. With one interesting exception, we have also been unable to detect the desorption of divalent ions. We did find that the dye, methyl green, would desorb. It is a divalent ion, but the charge is not localized and does not present as high a field strength to surrounding molecules. Thus, it should not have solvation energies as high as would be expected for species like  $\text{Ca}^{2+}$ . On the other hand, it may turn out that divalent ions do in fact desorb but that they take so many solvent molecules with them that the ion mass is too high to be seen with the spectrometers that have thus far been used in these experiments. We have recently obtained a new spectrometer that will extend our mass range to about 1500. Perhaps it will be able to provide some answers to this and other questions, some of which we do not yet know enough to ask.

### Reflections and Conclusions

Although the results that we have described must be considered as preliminary and incomplete, they seem to us to have many interesting and perhaps important implications. In the first place the electrospray-bath gas-free-jet ionization (ESPI) offers a method of producing new kinds of species for examination in vacuo by various spectroscopic methods. For example, there is a growing interest in the properties of matter in the form of small clusters. ESPI seems capable of generating such clusters with compositions that cannot be as readily realized by other methods. Large, complex, fragile, and otherwise nonvolatile molecules can be readily incorporated. By varying composition of the original solution and the bath gas one can "build" clusters containing such

involatile molecules in aggregation with any or many of the wide range of companion species. It is clear that the number of solvent molecules can be varied by adjusting the partial pressure of solvent vapor and the temperature of the bath gas. Precise control may be difficult because of possible condensation during the free-jet expansion, but though it might be a nuisance in some experiments that phenomenon could be put to good use in others. Even more intriguing is the possibility of bringing about more drastic changes in cluster composition by chemical reaction with various kinds of reagents in the bath gas prior to the free-jet expansion. A new chemistry of cluster structure and reactions might well follow, akin to what the flowing afterglow technique had made possible. Of course, all these considerations apply just as well to clusters of "simple" species, for example, the clusters comprising a proton or other cation in aggregation with methanol and water molecules that we described earlier.

Then there is the case of the degenerate cluster from which all solvent molecules have been removed to leave the bare core ion. Especially when fragile and nonvolatile molecules are in interest does ESPI provide an inviting route to spectrometric examination. The ion currents are likely to be small and the corresponding densities quite low but they are clearly large enough for mass spectrometry, should be large enough for laser induced fluorescence, and could be large enough for matrix spectroscopy. Intrepid investigators will no doubt figure out ways to apply other kinds of examination techniques. An important feature of ion species produced by ESPI is that they are almost sure to be in the ground state with respect to electronic and vibrational energy levels. Moreover the free-jet cooling should minimize rotational spread. Other methods of producing ions in vacuo often give rise to ions in highly excited states.

A third and perhaps most direct application of ESPI should be in that *sine qua non* of chemical science, analysis. Mass spectrometry has been one of the most sensitive, specific, and versatile methods of identifying and assaying compounds that the analytical chemist has had. Its combination with gas chromatography in so-called GC-MS has created a real revolution in the analysis of complex mixtures containing only trace amounts of some components. Unfortunately, mass spectrometric methods have not been nearly so effective in analyzing samples containing the complex or fragile organic molecules that are so important in biological systems and are assuming increasingly important roles in the process industries. In particular, the development of liquid chromatography over the past decade has created an intense interest in the possibility of mass spectrometric detection so that LC-MS could achieve for the analysis of liquid systems some of the wonders that GC-MS has wrought in gas-phase analysis. The major stumbling block in the application of mass spectrometry to liquid systems has been the problem of transforming nonvolatile molecules from their initial conditions as solutes in a liquid solution to ions in vacuo ready for mass analysis. There is an alphabet soup of ionization methods that mass spectrometrists have used including electron bombardment ionization (EI), chemi-ionization (CI), atmospheric pressure ionization (API), and photoionization (PI or MPI). All of these methods usually require that the molecule be in the vapor phase to start with. Moreover, they frequently result in substantial fragmentation of the parent molecule. There have also been a number of relatively recent methods aimed specifically at the problem of dealing with nonvolatile species. Among them are field desorption ionization (FI),<sup>28-30</sup> laser desorption ionization (LDI),<sup>31,32</sup> secondary ion mass spectrometry (SIMS),<sup>33</sup> fast atom bombardment ionization (FAB),<sup>34,35</sup> and plasma desorption ionization (PDI).<sup>36,37</sup> These

techniques have shown some effectiveness under some conditions but none of them represent really general and convenient methods of producing ions from nonvolatile molecules. Most of them result in appreciable fragmentation of the parent molecule. In particular, none of them has provided the basis for an effective interface between a liquid chromatograph and a mass spectrometer.<sup>38</sup> Recently, however, substantial progress on the LC-MS problem has been achieved by Vestal and his collaborators with their remarkable thermospray (TS) ion source.<sup>42-44</sup> In common with ESPI and the APIE source of Thomson and Iribarne, TS seems to depend upon field desorption of ions from evaporating charged droplets. As in APIE the charged droplets are produced by atomizing an ionic solution but the atomization is effected simply by passing the solution through a heated tube. A substantial fraction of the solvent is vaporized and the resulting droplet-laden vapor emerges from the tube into an evacuated region as a supersonic jet. A side stream of vapor carrying desorbed ions passes through a small orifice into the mass spectrometer chamber. This TS source has been successfully interfaced with a liquid chromatograph and has produced in vacuo intact solute ions having masses over 1700 with remarkable effectiveness.

We believe that the results we have obtained with ESPI in light of the theory and experiments of Dole and his colleagues,<sup>1-5</sup> Stimpson et al.,<sup>24-26</sup> and especially Iribarne and Thomson,<sup>22,23</sup> open up an extremely promising approach to mass spectrometric analysis of samples containing organic molecules that are too large, complex, involatile, or fragile for ionization by conventional methods. We are eagerly pursuing this approach.

The Iribarne-Thomson desorption model seems to be the best explanation for the origin of the ions we see. Implicit in its mechanism is the likelihood that the composition of these ions reflects the nature of the solution from which they come. Consequently, a study of the dependence of ion composition on solution composition and electrospray parameters might well give new insight on the structure and properties of solutions. In particular, because desorption must occur at the surface of the solution, the composition of the desorbed species may comprise a probe by which surface composition and structure may be studied. Of course, en route to the mass spectrometer the desorbed ions are exposed to a wide range of conditions so that the actual composition finally seen does not relate all that directly to the composition of the ion as it is desorbed. However, it should be possible to draw some inferences about the initial composition if examination is carried out over a sufficiently wide range of experimental conditions. Moreover, the behavior and properties of the clusters *per se* should reveal much about the liquid state because they represent a stage intermediate between the gaseous state that we understand relatively well and the liquid state that we know much less about. The pioneering studies of Kebarle exemplify what can be done by such an approach.<sup>39</sup>

Finally, it is appropriate to reexamine the Dole experiments that stimulated our initial interest in the electrospray process. We set forth earlier the logic that forced us to abandon the notion that individual solute ions could simply be the residue resulting from a repeated sequence of evaporation of solvent from a charged droplet followed by subdivision due to Rayleigh instability. The same kind of arithmetic seems to rule out that possibility in Dole's experiments. In many cases there were more macromolecules than charges in the electrospray flux. Thus, it would seem that ions comprising individually charged macromolecules would have to result from an ion desorption process of the kind invoked by Iribarne and Thomson. Perhaps we are unduly suspicious but we

(34) D. J. Surman and J. C. Vickerman, *J. Chem. Soc., Chem. Commun.*, 324 (1981).

(35) M. Barber, R. S. Bordoli, R. D. Sedgwick, and A. N. Tyler, *J. Chem. Soc., Chem. Commun.*, 325 (1981).

(36) R. D. Macfarlane and D. F. Torgerson, *Int. J. Mass Spectrom. Ion Phys.*, **21**, 81 (1976).

(37) C. J. McNeal and R. D. Macfarlane, *J. Am. Chem. Soc.*, **103**, 103 (1981).

(38) P. J. Arpino, *Biomed. Mass Spectrom.*, **9**, 176 (1982)

(39) P. Kebarle, "Ion-Molecule Reactions", Vol. 1, Plenum Press, New York, 1972, p 315.

(28) H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 500 (1969).

(29) H. D. Beckey, "Principles of Field Ionization and Field Desorption Mass Spectrometry", Pergamon Press, Oxford, 1977.

(30) J. F. Holland, B. Soltmann, and C. C. Swedey, *Biomed. Mass Spectrom.*, **3**, 340 (1976).

(31) M. A. Posthumus, P. G. Kistemaker, H. L. C. Meuzelaar, and M. C. Ten Noever de Brauw, *Anal. Chem.*, **50**, 985 (1978).

(32) R. Stoll and F. W. Rollgen, *Org. Mass Spectrom.*, **14**, 642 (1979).

(33) A. Benninghoven, D. Jaspers, and W. Sichtermann, *Appl. Phys.*, **11**, 35 (1976).



are bothered by the idea that ions with molecular weights of tens to hundreds of thousands and a single charge could desorb from a droplet surface. Moreover, we are bothered by some other features of the experiments and their interpretation. Along with the authors we find it difficult to understand why the repeller voltage at which ion transmission begins to decrease should decrease as the concentration of solute macromolecules decrease. This behavior can only mean that the ion mass is decreasing and that, therefore, at the higher solute concentrations the ions must contain more than one macromolecule. The assumption that we find most difficult to accept is that the final macroion velocity equals the terminal carrier gas velocity. Molecules much smaller than those used by Dole and his colleagues show "slip" effects resulting in substantial velocity deficits. Miller and Andres have developed a "slip Knudsen number" parameter that successfully correlates the experimental results of Abuaf et al.<sup>40,41</sup> Even

optimistic estimates of the value of this parameter for Dole's experiments indicate that the macroions must have a velocity much less than the velocity of gas. In view of these considerations, we are inclined to think that at least some of Dole's ions might well have comprised aggregates of macromolecules carrying more than one charge. Even so, his conception of the electrospray-bath gas-free-jet combination remains a powerful and important contribution.

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(40) N. Abuaf, J. R. Anderson, R. P. Andres, J. B. Fenn, and D. R. Miller, "Rarefied Gas Dynamics, 5th Symposium", C. L. Brundin, Ed., Vol. 2, Academic Press, New York, 1966, p 1317.

(41) D. R. Miller and R. P. Andres, "Rarefied Gas Dynamics, 6th Symposium", L. Trilling and H. Wachman, Ed., Vol. 2, Academic Press, New York, 1969, p 1385.

(42) C. R. Blakley, J. J. Carmody, and M. L. Vestal, *Anal. Chem.*, **52** 1636 (1980).

(43) E. O. Hardin and M. L. Vestal, *Anal. Chem.*, **53**, 1492 (1981).

(44) C. R. Blakley and M. L. Vestal, *Anal. Chem.*, **55**, 750 (1983).

## Pulsed Free Jets: Novel Nonlinear Media for Generation of Vacuum Ultraviolet and Extreme Ultraviolet Radiation

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We describe the application of free jets for the frequency tripling of laser radiation. Using a supersonic expansion of Xe we obtain  $\sim 5 \times 10^{11}$  photons/pulse at 118.2 nm for an input power of 18 MW at 354.7 nm, while for CO we obtain  $\sim 1 \times 10^{12}$  photons/pulse at 98.5 nm for an input power of 2 MW at 295.6 nm. In the latter case the conversion efficiency is enhanced by a two-photon resonance via the CO A<sup>1</sup>Π state. A simple model is presented for third harmonic generation in a free jet, and the predictions of this model are tested against experiment.

### Introduction

Modern lasers provide intense, tunable, and essentially monochromatic light from the near-infrared to the ultraviolet. These sources have been extensively applied to chemical studies, greatly extending our knowledge of molecular spectroscopy, photochemistry, and state-selective reaction dynamics. However, many important molecular species (e.g., H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, CO) have their lowest electronically excited states in the vacuum ultraviolet (VUV), below  $\sim 185$  nm. In order to apply laser techniques to study the spectroscopy and photochemistry of such species, and to access the Rydberg states of most molecules, it is necessary to develop tunable laser sources for this region. Unfortunately, the range of lasers operating in the VUV is rather restricted. Laser action has been demonstrated for only a handful of species, most notably H<sub>2</sub>, F<sub>2</sub>, CO, and the excimers of Xe, Kr, and Ar.<sup>1</sup> Furthermore, these can only operate on discrete lines and are consequently of limited value. For broadly tunable sources, a better approach is to frequency upconvert a high-power dye laser.

Frequency mixing and harmonic generation are well established as means of wavelength extension for visible lasers.<sup>2,3</sup> Typically, noncentrosymmetric crystals are employed as the upconverting

(nonlinear) medium. However, the crystals in current use are all optically opaque below about 195 nm and therefore cannot be used for VUV generation. Instead it is necessary to employ gaseous nonlinear media,<sup>4-10</sup> such as rare gases or metal vapors. Numerous schemes have been described for the generation of coherent light throughout the VUV and even below the lithium fluoride cutoff (104 nm), in the extreme vacuum ultraviolet (XUV).<sup>11-17</sup> Some

(1) S. C. Wallace, *Adv. Chem. Phys.*, **47**, 153 (1981).

(2) P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, *Phys. Lett.*, **7**, 118 (1961).

(3) M. D. Levenson, "Introduction to Nonlinear Laser Spectroscopy", Academic Press, New York, 1982.

(4) J. F. Ward and G. H. C. New, *Phys. Rev.*, **185**, 57 (1969).

(5) A. H. Kung, J. F. Yound, G. C. Bjorklund, and S. E. Harris, *Phys. Rev. Lett.*, **29**, 985 (1972).

(6) R. B. Miles and S. E. Harris, *I.E.E.E. J. Quantum Electron.*, **QE-9**, 470 (1973).

(7) A. H. Kung, J. F. Young, and S. E. Harris, *Appl. Phys. Lett.*, **22**, 301 (1973); **28**, 239 (E) (1976).

(8) R. T. Hodgson, P. P. Sorokin, and J. J. Wynne, *Phys. Rev. Lett.*, **32**, 343 (1974).

(9) A. H. Kung, *Appl. Phys. Lett.*, **35**, 653 (1974).

(10) K. K. Innes, B. P. Stoicheff, and S. C. Wallace, *Appl. Phys. Lett.*, **29**, 715 (1976).

(11) R. Hilbig and R. Wallenstein, *Opt. Commun.*, **44**, 283 (1983).

(12) E. E. Marinero, C. T. Rettner, R. N. Zare, and A. H. Kung, *Chem. Phys. Lett.*, **95**, 486 (1983).

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