

Studies of Ions in a Drift Field: Laser Diagnostics of Excited States and
Measurements of Thermochemical Properties at Equilibrium

NOTICE

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Knowledge of the behavior and properties of ions drifting in gases at high pressures has wide-ranging implications to a number of basic and applied areas ranging from the field of interface physics, which is just beginning to lay a foundation for connecting the properties of gaseous and condensed phases, to applications such as radiation and nuclear reactor chemistry, combustion processes, and the chemical and physical processes taking place in the earth's environment. All of these depend on attaining a more complete understanding of the properties of the ions, their degree of excitation in the presence of a drift field, and their attainment of an equilibrium distribution which enables measurements of their properties to be uniquely defined.

A major technique for investigating the thermochemical properties of ions and their related clusters is the high pressure drift/mass spectrometer detection technique which has been utilized in our laboratory for a number of years and has provided extensive information on the bonding of various polar and nonpolar molecules to ions, with concomitant information being attained on the depth of the well of interaction between ions and molecules, and related inferences concerning the structure of these stable gas-phase complexes. A crucial question in this regard is the extent to which ions drifting in an electric field are thermalized, thereby attaining a Boltzmann distribution from which thermochemical properties can be derived. This paper is divided into two parts, one describing some new laser techniques which are enabling an investigation of the possible presence of excited ions in a drift field, and secondly, a reporting of some recent findings and trends in the stability of ion clusters of single and mixed constituents.

LASER DIAGNOSTICS OF IONS IN A DRIFT FIELD

In recent years, we have developed a technique for studying the laser photodissociation of ions and ion clusters extracted from a high pressure ion drift cell [1]. The method enables a detailed investigation of the photodissociation cross sections of the ions and their complexes, thereby allowing a direct measurement to be made of the extent to which electric fields within the drift cell influence the photodissociation cross sections and the spectral features such as rotational and vibrational states of the ions. The method also enables information to be acquired on the dynamics of photodissociation, energy transfer, and spectroscopic information related to the structure of the complexes themselves. Herein, attention is focused on the photodissociation of CO_3^- to O^- as an example of the power and utility of the technique.

Basically, the apparatus consists of an ion drift source, a system of ion optics, Wien filter, a Faraday probe, a laser interaction region, a retarding field energy analyzer, and a quadrupole mass spectrometer for measurement of

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product mass and intensity. Photodissociation is attained using a tunable cw dye laser pumped with an argon ion laser; the commercial dye laser has been substantially modified enabling the ion beam to pass through the cavity of the dye laser. The ion drift source has provisions for controlling the energy of the ions which are studied in the experiments. In the case of CO_3^- , ions are produced in the source by interaction of electrons omitted from the filament with a suitable gas mixture comprised of N_2O , CO_2 , and H_2O in varying proportions. O^- is generated from N_2O and the desired ions and hydrates are produced via a series of association reactions. The Wien filter serves to mass select the desired ion for introduction into the laser/ion interaction region which is accurately located using the Faraday probe. Following interaction of the ions with the intracavity light of the dye laser, the product ions are accelerated into the quadrupole mass spectrometer.

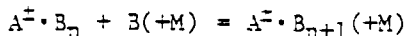
A typical photodissociation spectrum taken at low field energies ($E/p \sim 20$ V/cm-torr) is shown in the lower curve of Figure 1, in good agreement with observations reported by others [2,3]. At moderate fields, the photodissociation spectrum becomes significantly altered due to the ions being vibrationally excited.

A very definitive observation of the influence of the electric field on relative cross section was observed at even higher field energies. Near 100 V/cm-torr an anode plasma condition was attained having the properties characteristic of a glow discharge, e.g., there was hysteresis in the attainment and loss of this condition with regard to the electric field imparted to the drift cell. CO_3^- produced in this anode plasma had a structureless photodissociation spectrum with cross sections more than an order of magnitude higher than CO_3^- generated at low field conditions. Rather dramatic evidence for the influence of drift fields on the ions is seen by a moderately high resolution photodissociation experiment on one of the vibration bands where rotational resolution was attained. The low field condition of $E/p = 19$ V/cm-torr displays a rather narrow band with well defined rotational structure. At moderate field energies $E/p = 44$ V/cm-torr, the band becomes significantly broadened and the relative photodissociation cross section is slightly increased (see Figure 2). This is in agreement with the propensity of high rotational states to undergo photodissociation.

The power of this technique, not only in assessing the influence of drift fields but also the influence of collisional excitation and the failure for ions to sufficiently relax following production even at zero field conditions. One can expect such methods to play a much more prominent role in the field of ion swarms and in the general area of ion-molecule reactions.

THERMOCHEMICAL PROPERTIES OF ION CLUSTERS UNDER EQUILIBRIUM CONDITIONS

The high pressure drift cell/mass spectrometer technique for measuring the thermochemical properties of association reactions has been extensively developed and utilized in our laboratory [4] for reactions of the type



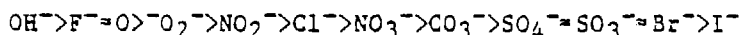
Here, A^{\pm} designates a positive or negative ion, B the clustering neutral (ligand), and M the third-body necessary for collisional stabilization of the complex. Taking the standard state to be 1 atm, and making the usual

assumptions [4] concerning ideal gas behavior and the proportionality of the chemical activity of an ion cluster to its measured intensity, the equilibrium constant $K_{n,n+1}$ is given by

$$\ln K_{n,n+1} = \ln \frac{I_{n+1}}{I_n P_B} = - \frac{\Delta G^\circ_{n,n+1}}{RT} = - \frac{\Delta H^\circ_{n,n+1}}{RT} + \frac{\Delta S^\circ_{n,n+1}}{R}$$

Here, I_{n+1} and I_n represent the respective measured ion intensities, P_B the pressure (in atm) of clustering molecules B, $\Delta G^\circ_{n,n+1}$, $\Delta H^\circ_{n,n+1}$, and $\Delta S^\circ_{n,n+1}$ the standard Gibbs free energy, enthalpy, and entropy changes, respectively, R the gas-law constant, and T absolute temperature. The technique permits clustering to be investigated sequentially, whereby details of the enthalpy of clustering can be obtained from slopes of van't Hoff plots and entropies from appropriate intercepts. Numerous experimental tests are made to establish the attainment of equilibrium in the drift cell. One of these pertains to the influence of the electric field where low field conditions are found from a condition where the equilibrium constant is independent of E/p (see Figure 3). Data have been determined for numerous negative and positive ion complexes in our laboratory [4-11].

The results of the present studies have led to an understanding of factors controlling the strength of the bonding of various neutrals to ions both with regard to the role of the ion and of the neutral. The results show that the strength of the bonding of the ions with the three neutrals CO_2 (a non-polar molecule), H_2O (a protic polar molecule), and SO_2 (a aprotic polar molecule) is consistent with the inequality



This relationship appears to parallel the order of the gas phase basicity of the negative ions where the strongest bases exhibit the largest bond dissociation energies (see Reference 5).

Another interesting finding of our work is seen by comparing the relative bond dissociation energies, $D(\text{A}^--\text{B})$ for a given ion, with the different ligands SO_2 , H_2O , and CO_2 . The trends are in accord with expectations based on electrostatic considerations, where polarizability of the neutral dominates for small ions while permanent moments govern stability for larger ions (see References 5 and 12).

The thermodynamic parameters derived for positive ion-neutral complexes have provided unique information on the strength of bonding and structure of these complexes too. In addition, structural computations using quantum mechanical and electrostatic theories have provided further insight into the nature of bonding and arrangement of ligands about the central ion. Details of the solvation process of various ions [12,13], evidence to support proposed identifications of cluster species in the atmosphere [14], and extended understanding of transition metal complexes [8] have resulted from the investigations.

A strong dependence on ionic radius is observed upon comparing strengths measured for the first ligand-ion bonds for the case of the alkali metal ion series [4]. This would be expected for systems having essentially only electrostatic contributions to their bonding. Our work on the clustering of molecules to the transition metals Ag^+ and Cu^+ have shown that the first ligand binds to these ions much more strongly than to ones in the alkali metal series [8]. Based on extended Huckel calculations performed in our laboratory, the presence of partial covalent hybrid bonding explains the larger enthalpies of ammoniation relative to hydration for the alkali metal ions [4]. A number of important findings have been derived from our recent studies of the successive ligand clustering to ions. The observation of breaks in plots of successive enthalpy change as a function of the number of ligands has been a valuable illustration of the formation of coordination shells about ions in the gas phase having analogies to solvation breaks observed in the condensed phase [4,8,11,15,16].






Since the sodium ion is a spherical closed shell entity of intermediate size, differences in the bonding of a variety of clustering ligands to this ion reflect properties intrinsic to the individual ligands. A comparison of these results for ligands attached to a particular ion also allows one to probe the bonding characteristics of that ion.

The series of neutral ligand molecules chosen for this study include both the polar species H_2O , NH_3 , SO_2 , and CO , as well as the non-polar ones CH_4 and CO_2 . Since the bonding interactions to alkali metal ions are expected to be primarily electrostatic in nature, trends in the bonding strength should be directly related to similar trends in the dipole and higher moments.

Ordering the ligand molecules with respect to the enthalpy change involved in forming the first cluster shows that this is indeed the case. For the clusters investigated so far, this order is: $\text{DME} > \text{NH}_3 > \text{SO}_2 > \text{CO}_2 > \text{HCl} > \text{N}_2 > \text{CH}_4$ (where DME - dimethoxyethane - produces the largest enthalpy change due to the formation of a bidentate bond). The contribution of ion-induced dipole and ion-quadrupole interactions to the binding strength is indicated by the stronger bond for the ammonia cluster than for the water cluster. Although ammonia has the smaller dipole moment, its much larger polarizability and quadrupole moment further enhances its cluster stability. The role of the quadrupole is also seen by comparing the bonding of SO_2 with NH_3 . Both have approximately comparable values of dipole moments and polarizabilities, but the quadrupole moment of SO_2 leads to a repulsive interaction compared to the attractive one of NH_3 , consistent with the much decreased bonding strength of SO_2 .

An examination of the bonding of neutral molecules onto ions in the gas phase has particular value in elucidating the properties which determine the ligand's ability to cluster onto ions. For this purpose, the association of ammonia, water, sulfur dioxide, and carbon dioxide with both Na^+ and Cl^- has been investigated. The ion-dipole interaction is the most important electrostatically attractive force between an ion and a neutral molecule. Both sodium and chloride ions have closed electronic configurations and spherical symmetry, although the ionic radius of Na^+ is considerably smaller. Consequently with other factors equal, a neutral molecule would be expected to bind more strongly to Na^+ . However, factors such as quadrupole moment, polarizability, hydrogen bonding, and charge transfer may also be important. Table I lists some of the relevant electrostatic properties of the neutral molecules considered here.

Table I. Electrostatic Properties

Molecule	Dipole Moment D (Debye)	Quadrupole Moment			Polarizability			Axes 
		Q_{zz}	Q_{yy}	Q_{xx}	α_x	α_y	α_z	
H ₂ O	1.85	-0.26	-3.0	3.26	1.45	1.65	1.23	
SO ₂	1.63	2.6	3.0	-10.6	2.65	4.27	4.17	
NH ₃	1.47	-4.64	3.32	3.32	2.39	2.1	2.1	
CO ₂	0	-8.64	4.32	4.32	4.05	1.95	1.95	

The experimentally determined stepwise heats of association are given in Table II. Some interesting comparisons are immediately apparent: (1) only sulfur dioxide binds more strongly to Cl⁻ than Na⁺ for the first association step, (2) ammonia exhibits the largest difference between Na⁺ and Cl⁻, (3)

Table II: Stepwise heats of association, $-\Delta H^\circ_{n,n+1}$, in kcal/mole for $I \cdot B_n + B \rightleftharpoons I \cdot B_{n+1}$.

n	I	(n, n+1)					
		(0,1)	(1,2)	(2,3)	(3,4)	(4,5)	(5,6)
H ₂ O	Cl ^{-a}	14.9	12.6	11.3	10.9	—	—
	Na ⁺ b	24.0	19.3	15.3	13.3	12.3	10.7
SO ₂	Cl ^{-a}	21.8	12.3	10.0	3.5	—	—
	Na ⁺ c	18.9 ^e	16.5 ^d	14.3 ^d	—	—	—
NH ₃	Cl ^{-a}	3.2	—	—	—	—	—
	Na ⁺ d	29.1	22.9	17.1	14.7	10.7	9.7
CO ₂	Cl ^{-a}	3.0	—	—	—	—	—
	Na ⁺ d	15.9	11.0	9.7	—	—	—

^aKeenan et al., 1980

^dCarson, 1982

^bOzidic and Kebabla, 1970

^eThis work

^cPerry et al., 1980

^fCasclaman et al., 1978b

the relative stability of the ion-molecule complexes for NH₃, H₂O, and SO₂ are in reverse order for the two ions, and (4) the absolute magnitude of the enthalpy changes for the additional clustering of SO₂ onto Cl⁻ are smaller than for Na⁺.

Many of these trends are in agreement with expectations from electrostatic properties. For instance water, sulfur dioxide, and ammonia have similar dipole moments; however, when the dipoles are aligned in the

electrostatic field of the ion, the small quadrupole moments (Q_{zz}) of water and the considerably large one of ammonia are repulsive to a negative charge and attractive to a positive one. In the case of sulfur dioxide, the situation is reversed. Thus, the ion-quadrupole interaction is consistent with the different ordering of $-\Delta H^{\circ}_{0,1}$ for water, ammonia, and sulfur dioxide between the positive ion Na^+ and the negative ion Cl^- . From electrostatic considerations, $\text{Na}^+\cdot\text{CO}_2$ is expected to be a linear complex (Q_{zz} attractive) and $\text{Cl}^-\cdot\text{CO}_2$ should be a T-complex (Q_{yy} and Q_{xx} attractive). As has been shown earlier [5], charge transfer or covalent bonding is an additional consideration in the binding of CO_2 and particularly SO_2 with Cl^- . This covalency increases the stability of the $\text{Cl}^-\cdot\text{SO}_2$ complex but decreases subsequent clustering due to the dispersal of charge over the SO_2Cl^- ion.

An interesting application is the recent development of a correlation which relates these gas phase clustering data to properties of ions present in a solvent medium. In particular, we have found that the ratio of the enthalpy of solvation in the condensed phase to the summed enthalpy of clustering from gas phase measurements rapidly converges with respect to clustering number [13]. This fact has been observed in our laboratory for the case of various atomic, as well as complex molecular negative ions in the case of hydration, and in the case of ammoniation and hydration of positive ions. It was found that the single ion heat of solvation values could be deduced from knowledge of the first six cluster bond energies measured in the gas phase. These findings suggest that it may be possible to utilize gas phase experiments for elucidating the molecular aspects of the condensed phase for other systems as well.

Studies of mixed clusters provide insight into potential interactions between the ligands attached to the ion. Questions have been raised regarding the influence of the ion on the ligand charge density and its effects on subsequent clustering, and in regard to possible interactions between ligands. Thermodynamic results for the $\text{Na}^+/\text{H}_2\text{O}/\text{CO}_2$ system and some preliminary results for the $\text{Na}^+/\text{H}_2\text{O}/\text{SO}_2$ system have been obtained. While it is somewhat more difficult to obtain appropriate experimental conditions for the study of mixed clusters, the results have proven quite interesting.

Some small degree of partial covalent bonding, observed commonly with transition metal ions, appears to occur even for the simple alkali metal ions. This has been determined through a comparison of the experimental results for the clustering of CO_2 to Na^+ with electrostatic calculations. The first neutral molecule bonds more strongly than predicted, the stability dropping rapidly as additional ligands are added. This behavior indicates a transfer of charge density from the CO_2 to the Na^+ , decreasing the interaction potential attracting the second CO_2 molecule.

The mixed cluster system $\text{Na}^+(\text{H}_2\text{O})_n\text{CO}_2$ also illustrates the influence of covalent character on the primarily electrostatic bonding. Electrostatic predictions suggest that CO_2 addition to $\text{Na}^+\cdot\text{H}_2\text{O}$ is less favorable than to $\text{Na}^+\cdot\text{CO}_2$ due to greater ligand-ligand repulsion in the former case. This is contrary to experimental results which show the values to be nearly equal.

To interpret the relative stability of mixed clusters with an equal number of total ligands, energy scales for the free energy and enthalpy changes of clustering as a function of composition (expressed as m/n) have

been constructed. The mixed clusters $\text{Cl}^-(\text{H}_2\text{O})_n(\text{SO}_2)_m$ show deviations toward greater stability compared to the tie-lines between the pure clusters ($\text{Cl}^-(\text{H}_2\text{O})_{n+m}$ and $\text{Cl}^-(\text{SO}_2)_{n+m}$) whereas $\text{Na}^+(\text{H}_2\text{O})(\text{SO}_2)$ shows a deviation in the opposite direction for the enthalpy change of clustering and essentially no deviation for the free energy. Earlier results for the mixed clusters $\text{Na}^+(\text{H}_2\text{O})_n\text{CO}_2$ show slight deviations toward greater stability. Considering results from other laboratories, $\text{H}^+(\text{H}_2\text{O})(\text{H}_2\text{S})$ shows no deviations whereas $\text{H}^+(\text{H}_2\text{O})_n(\text{H}_2\text{S})_m$ with $n+m=3$ shows deviations toward greater stability and $\text{H}^+(\text{H}_2\text{O})_n(\text{NH}_3)_m$ ($n+m \leq 5$) also shows substantial deviations in this direction. One should note that in none of these systems has a mixed cluster shown heats of clustering greater than the stabler of the two single constituent clusters.

ACKNOWLEDGMENTS

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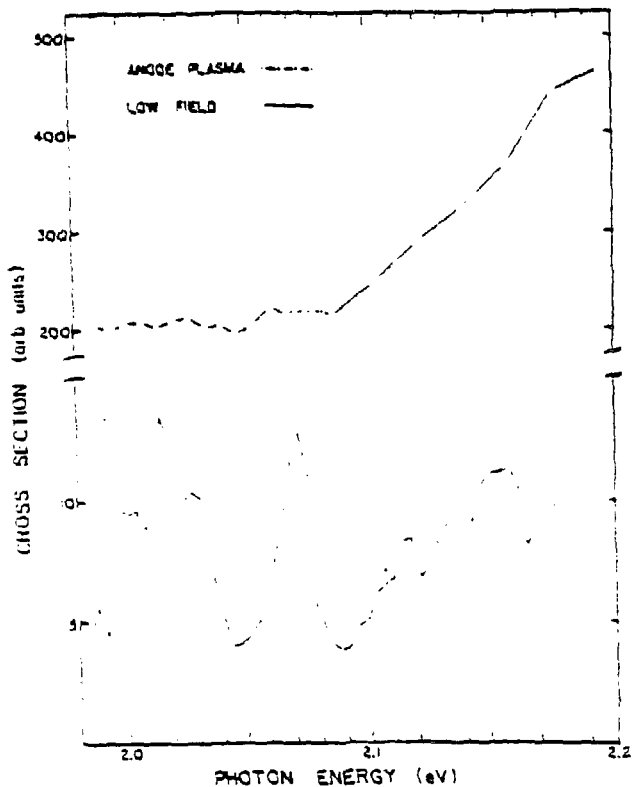


Fig. 1. Spectra taken under different source electric field conditions. Low field drift condition shows well-resolved ground state structure, whereas attainment of the anode plasma condition leads to the great enhancement of cross section of all wave-lengths with loss of structure.

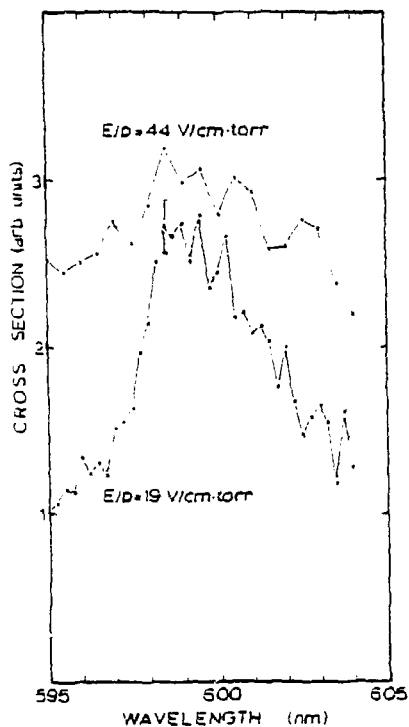


Fig. 2. Higher resolution CO_3^- Photo-dissociation spectra showing the influence of ion source electric field on cross sections.

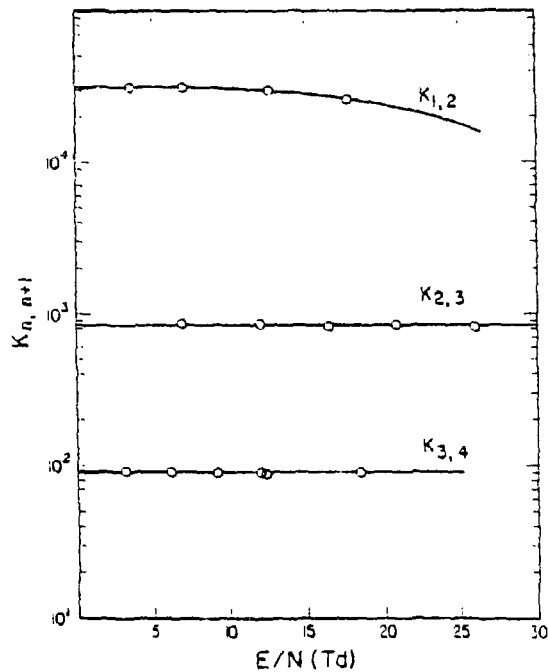


Fig. 3. Data for the clustering of ammonia to Li^+ showing the independence of the equilibrium constant at low values of electric field, where $E/N(\text{Td}) = 2.83 E/p$ (v/cm-torr).

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