







Technical Note

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Survey of Multiply Charged Ions

Fred L. Mohler*

This is a survey of experimental results on multiply charged rare gas ions, molecule ions and radical ions with emphasis on simpler compounds that may be of astrophysical interest. Tables of rare gas ions, simple molecules and a few hydrocarbon molecules include data on relative abundance and appearance potentials of the ions.

1. Introduction

Interest has been expressed in the occurrence of multiply charged molecule ions and rare gas ions that are observed or could be expected in atmospheres of planets and stars. Wilkinson [1] listed possible molecules, atoms and radicals as; rare gases, N_2 , O_2 , NO, NH_3 , NH_2 , oxides of carbon, CH_4 , C_2H_2 , C_2H_4 , CH_2 , C_2H , C_2 , C_3 , CN, H_2O , HCN and SiC_2 . Mrs. Charlotte Moore Sitterly suggested that there is also interest in BO, N_2O , N_2O_4 , TiO, BH, AlH, MgH, SiH, CaH, SiF, and ZrO. OH has recently been reported in the radio spectrum of a nebula. Many of these compounds are radicals rather than molecules. This is true of NH_2 , CH_2 , C_2H , SiC_2 , BO, OH, the listed metal mono-hydrides; SiF and ZrO. In the case of radicals one can look for the doubly charged radical ion as a product of ionization of a molecule.

I have included doubly charged ions of a number of other simple compounds in this report as the interest in this subject is not limited to astrophysics.

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Rare gas ions of multiple charge have been identified and classified spectroscopically for all the rare gases [2]. Research on multiple ionization of atoms and molecules by electron collision has been stimulated by theoretical studies by Wannier [3] and Geltman [4]. They indicate that the probability of n-fold ionization will increase above the threshold as the nth power of the excess voltage above the threshold. The excitation function begins to round off within 10 volts of the threshold and approaches a flat maximum within 100 volts.

In the preparation of this report, the book by Field and Franklin on electron impact phenomena [5] has been a valuable assistance. It gives a quite complete survey of all experimental work on the subject up to 1957. A paper by Dorman and Morrison on double and triple ionization of molecules [6] published in 1961 in J. Chem. Phys. was also very helpful. In view of the fairly complete coverage of data to 1961, I have not attempted to report all the research on this subject but list for each molecule only the results of one or two researches which I consider to be the most accurate and most complete.

In the case of molecular ionization it requires mass spectrometric analysis to identify doubly charged molecular ions and in the case of simple symmetrical molecules this method may fail. Thus $N^{14}N^{14}2+$ will not be distinguished from N^{14+} . In recent years highly enriched heavy isotopes of the common gases have been available and one can study unsymmetrical molecules such as $N^{14}N^{15}$, $O^{16}O^{17}$ and deuterioacetylene CH-CD to distinguish doubly charged molecules of apparent mass 14.5 16.5 and 13.5 from singly charged fragment ions.

Relative abundance is expressed in a variety of ways. API tables

[7] give abundance at 70 volts relative to the maximum peak in the mass spectrum. Others use the abundance at some other fixed voltage or at the maximum of the excitation function. While abundance is commonly expressed in terms of the ion current, Fox [8], [9] gives abundance in terms of the relative number of ions at the maximum of the excitation function. Thus the number of doubly charged ions is proportional to the current ratio divided by 2.

2. Results

Table 1 lists data on the rare gas ions. Spectroscopic values of the appearance potentials are available to Ne^{6+} , Ar^{9+} , Kr^{3+} and Xe^{5+} . In recent years there have been a number of mass spectrometric studies of rare gas ions and the choice of data cited in table 1 is rather arbitrary. Fox [8,9] as noted above compares the number of ions and Melton [11] compares ion currents at 3.5 KeV.

Tables 2 and 3 give data for simple molecules and some hydrocarbons. Column one gives the chemical formula of the molecule, column 2 the formula of the ion, column 3 the abundance, column 4 the appearance potentials and column 5 references. Double entries in column 4 are double series limits. Experimental errors given in these tables are values given by the authors.

Only a few hydrocarbons are listed in table 3 as interest was primarily in simple molecules. There are fairly complete data on abundances of the molecule ions and fragment ions of C_2 hydrocarbons.

Table 2 lists data for simple inorganic molecules. Direct experiments on the appearance potentials of N_2^{++} and O_2^{++} are complicated by the impossibility of distinguishing atom ions from doubly charged

molecules in symmetrical N_2^{14} and O_2^{16} . Quite recently there has been research on the appearance potentials of $N^{14}N^{15++}$ at m/e 14.5 [12,6] and $O^{16}O^{17}$ at m/e 16.5 [12].

There are some significant omissions from this table. Of the halogen acids all but HF give doubly charged ions and Dorman and Morrison [6] find HF^{++} less than 10^{-6} of HF^+ . Of the halogen molecules F_2 and I_2 are monoisotopic and F_2^{++} and I_2^{++} cannot be distinguished from F^+ and I^+ by a mass spectrometer. Dorman and Morrison [6] also find H_2O^{++} less than 10^{-6} and undoubtedly the same applies to OH^{++} for a mass peak of 8 1/2 would not escape observation.

Some qualitative observation of carbon ions are included in the table. These and heavier ions to C_9^{++} are obtained in a vacuum spark discharge between graphite electrodes. Chupka and Inghram [28] ionized carbon evaporated from incandescent carbon and found C^+ , C_2^+ and C_3^+ in the ratios 1 to .5 to 1.6 at 17 volts but did not look for doubly charged carbon molecules. Only a few hydrocarbons are listed in table 3 acetylene, ethylene and ethane, benzene, methyl benzene and naphthalene. It is convenient to use monodeutero compounds for then the doubly charged molecule ions have half integer values. Data on the appearance potentials are incomplete.

This report is primarily concerned with the simpler compounds but a few remarks on other hydrocarbons are in order. Multiply charged molecule ions become relatively abundant in the fused ring aromatic compounds naphthalene, anthracene, phenanthrene, etc. [6,7]. In an early survey of doubly charged hydrocarbon compounds [25] it is pointed out that in compounds with 5,6 or 7 carbon atoms the more abundant

doubly charged ions come from molecules with most of the H atoms removed.

A qualitative explanation of this is that when electrons are removed from two radicals in a polyatomic molecule single bonds tend to be broken but double bonds do not. Mohler, Dibeler and Reese [30] have identified fragment ions from the disruption of doubly charged molecules by the kinetic energy gained from the Coulomb repulsion.

3. References

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Table I. Multiply Charged Ions of Rare Gases

Ion	Abundance	Ref.	Appearance Pot.	Ref.
He ⁺	1		24.58	Spect. [2]
He ²⁺	.0042	[8]	78.98	Spect. [2]
Ne ⁺	1.	[10]	21.56	Spect. [2]
Ne ²⁺	.11	[10]	62.63	Spect. [2]
Ne ³⁺	.003	[10]	126.13	Spect. [2]
Ne ⁴⁺			223.15	Spect. [2]
Ne ⁵⁺			349.45	Spect. [2]
Ne ⁶⁺			507.36	Spect. [2]
Ar ⁺	1.0	[9]	15.76	Spect. [2]
Ar ²⁺	.17	[9]	43.38	Spect. [2]
Ar ³⁺	.007	[9]	84.28	Spect. [2]
Ar ⁴⁺	.0008	[9]	144.07	Spect. [2]
Ar ⁵⁺	.0004	[11]	219.07	Spect. [2]
Ar ⁶⁺	.00006	[11]	310.37	Spect. [2]
Ar ⁷⁺	.00003	[11]	434.37	Spect. [2]
Ar ⁸⁺	.000008	[11]	577.83	Spect. [2]
Ar ⁹⁺			1000.4	Spect. [2]
Kr ⁺	1	[9]	14.00	Spect. [2]
Kr ²⁺	.21	[9]	38.56	Spect. [2]
Kr ³⁺	.06	[9]	75.46	Spect. [2]

(Continued)

Table I

Ion	Abundance	Ref.	Appearance Pot.	Ref.
Kr ⁴⁺	.008	[9]	147±2	[9]
Kr ⁵⁺	.001.008	[9,10]	218±10	[9]
Kr ⁶⁺	.002	[11]	350±10	[9]
Kr ⁷⁺	.0005	[11]		
Kr ⁸⁺	.00005	[11]		
Xe ⁺	1.0	[8]	12.12	Spect. [2]
Xe ²⁺	0.40	[8]	33.33	Spect. [2]
Xe ³⁺	.17	[8]	65.5	Spect. [2]
Xe ⁴⁺	.064	[8]	111.	Spect. [2]
Xe ⁵⁺	.019	[8]	187.	Spect. [2]
Xe ⁶⁺	.0022	[8]	255.±3	[8]
Xe ⁷⁺	.00017	[8]	390 ±10	[8]

Table II. Multiple Ionization of Simple Molecules

Molecule	Ion	Abundance Percent	Appearance Pot. e.v	Ref.
N ₂	N ¹⁴ _N ¹⁵⁺⁺		42.7, 43.8±1	12
		0.2	43.5	6
O ₂	O ¹⁶ _O ¹⁷⁺⁺		36.3±.5	12
NO	NO ⁺⁺	0.1	39.8	6
CO	CO ⁺⁺	3x10 ⁻²	41.8, 45.9	6
CO ₂	CO ₂ ⁺⁺	4x10 ⁻²	36.4, 41.9±.3	6
NH ₃	NH ₃ ⁺⁺	5x10 ⁻³	33.7, 36.8±.2	6
HCl	HCl ⁺⁺	7x10 ⁻³	35.5±.5	6
DBr	DBr ⁺⁺	0.1	33.2±.3	6
HI	HI ⁺⁺	0.1	30.0±.5	6
Cl ₂	Cl ₂ ⁺⁺		32.6	13
Br ₂	Br ₂ ⁺⁺		30.0	13
HCN	HCN ⁺⁺	0.88	40.3±1	14
CF ₄	CF ₃ ⁺⁺	0.58	45.5±.5	15
CF ₄	CF ₃ ⁺⁺	1.7	43.8±.3	16
CF ₄	CF ₂ ⁺⁺	1.35	44.1±.5	15
CF ₄	CF ₂ ⁺⁺	4.9	44.3±.5	16
CF ₄	CF ⁺⁺	6x10 ⁻²		16
CF ₃ Cl	CF ₂ Cl ⁺⁺	.6	38.8±.5	15
CF ₃ Cl	CFCl ⁺⁺	.7	41.0±.3	15
CF ₂ Cl ₂	CF ₂ Cl ⁺⁺		36.3±.5	15

Molecule	Ion	Abundance Percent	Appearance Pot. e.v	Ref.
CF_2Cl_2	CFCl_2^{++}		$36.5 \pm .5$	15
CFCl_3	CFCl_2^{++}	2.4	$34.5 \pm .3$	15
CFCl_3	CCl_2^{++}	3.0		15
CCl_4	CCl_3^{++}		33.1	15
CCl_4	CCl_2^{++}		34.2	17
SiF_4	SiF_3^{++}	1.12		16
SiF_4	SiF_2^{++}	3.75		16
SiF_4	SiF^{++}	.71		16
SF_6	SF_4^{++}	9.7	$40.6 \pm .5$	16
SF_6	SF_3^{++}	1.1		16
SF_6	SF_2^{++}	6.0	$46.5 \pm .5$	16
SF_6	SF^{++}	.68		16
SiCl_4	SiCl_3^{++}	4.9	$33.8 \pm .5$	18
SiCl_4	SiCl_2^{++}	.65	$37.3 \pm .5$	18
SiCl_4	SiCl^{++}	1.2	42 ± 1	18
B_2H_6	$\text{B}^{10}\text{B}^{11}\text{H}_2^{++}$.43		23
B_2D_6	$\text{B}^{10}\text{B}^{11}\text{D}_2^{++}$.40		24
SbCl_3	SbCl_2^{++}	5.2	32.1	27
SbCl_3	SbCl^{++}	4.5	34.8	27
AsCl_3	AsCl_2^{++}	3.0	33.1	27

Molecule	Ion	Abundance Percent	Appearance Pot. e.v	Ref.
PCl ₃	PCl ⁺⁺	2.4		27
CS ₂	CS ₂ ⁺⁺		27.4±.2	31
CS ₂	CS ₂ ⁺⁺⁺	.07	53.6±.5	31
COS	COS ⁺⁺	5.2		7
COS	COS ⁺⁺⁺	.0007		31
C ₂ N ₂	C ₂ N ₂ ⁺⁺⁺	.0005		31

Graphite C₃⁺⁺, C₄⁺⁺ and heavier ions in vacuum spark [26]

Table II addendum-negative results

HF⁺⁺, H₂O⁺⁺, OH⁺⁺, CH₄⁺⁺ are not observed and are less than 10⁻⁶ of the singly charged ion [6].

F₂⁺⁺ and I₂⁺⁺ are unmeasurable as they are indistinguishable from F⁺ and I⁺ and C₂N₂⁺⁺ is not reported as it is masked by CN⁺.

Table III. Multiply Charged Ions of Hydrocarbons

Molecule	Ion	Abundance Percent	Appearance Pot. e.v	Ref.
C ₂ HD	C ₂ HD ⁺⁺	2.70		19
Ethylenes				
C ₂ H ₃ D	C ₂ H ₃ D ⁺⁺	.28		20
C ₂ H ₄	C ₂ H ₃ ⁺⁺	.38		20
	C ₂ H ₃ ⁺⁺	.3	36.0	14
Ethanes				
C ₂ H ₅ D	C ₂ H ₅ D ⁺⁺	.01		21
C ₂ H ₅ D	C ₂ H ₅ ⁺⁺ and C ₂ H ₃ D ⁺⁺	.84		21
C ₂ H ₅ D	C ₂ H ₃ ⁺⁺ and C ₂ HD ⁺⁺	.09		21
C ₂ H ₆	C ₂ H ₅ ⁺⁺	.54		21
C ₂ H ₆	C ₂ H ₅ ⁺⁺		32.2±1.5	29
C ₂ H ₆	C ₂ H ₃ ⁺⁺	.06		21
C ₂ H ₂ D ₄	C ₂ HD ₄ ⁺⁺	.20		21
C ₂ H ₂ D ₄	C ₂ HD ₃ ⁺⁺	.59		21
C ₂ H ₂ D ₄	C ₂ HD ₂ ⁺⁺	.03		21
Benzene				
C ₆ H ₅ D	C ₆ H ₅ D ⁺⁺	2.0	26.0	6
C ₆ H ₅ D	C ₆ H ₅ D ⁺⁺⁺	10 ⁻⁴ %	44±5	6
Toluene				
C ₆ H ₅ CH ₃	C ₆ H ₅ CH ₃ ⁺⁺	0.1	24.5±2	6

Molecule	Ion	Abundance Percent	Appearance Pot. e.v	Ref.
$C_6H_5CH_3$	$C_6H_5CH_3^{+++}$	$10^{-7}\%$	42 ± 5	6
Naphthalene				
$C_{10}H_8$	$C_{10}H_8^{++}$.2	$22.8 \pm .2$	6
$C_{10}H_7D$	$C_{10}H_7D^{++}$	12.		19
$C_{10}H_7D$	$C_{10}H_7D^{++}$		22.7	22
$C_{10}H_8$	$C_{10}H_8^{+++}$	3×10^{-5}	40 ± 5	6

