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Negative Ions Formed by Vacuum Spark Discharge. III.[1)] Polyatomic Negative Ions of the Elements in A-Subgroups on the Periodic Table

Hiroshi Kishi†

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

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Polyatomic negative ions for almost all of the elements in A-subgroups on the periodic table were tested by the spark discharge type ion source mass spectroscopy. A large number of polyatomic negative ions such as "polymer" negative ions, hydride negative ions, oxide negative ions, and carbide negative ions, could be detected. The results are discussed with reference to the reported values of electron affinities of the molecules and to the reported results by other methods of formation.

A study on negative ion spark source mass spectroscopy using a Mattauch-Herzog type double focusing mass spectrograph has been carried out. Formation of atomic negative ions of 48 elements has previously been reported,[2)] and the relative sensitivity coefficients for negative ions has also been reported.[1)]

The significant features of the Mattauch-Herzog type double focusing mass spectroscopy[3)] are (1) all ions of a given mass (m/z) range can be detected at the same time on a photographic emulsion plate, and (2) by the cumulative nature of the ion detection on the photographic emulsion plate, it is possible to detect ions of weak intensity: the exposure time is long and all ions formed during the exposure time are collected. In the experiment of atomic negative ions with the use of a spark discharge type ion source,[2)] a large number of polyatomic negative ions were detected in addition to the atomic negative ions.

On the polyatomic negative ions detected by spark source mass spectroscopy, there are only a few reports in the literature.[4,5)] This might reflect the difficulty of the formation of negative ions by spark discharge type ion sources, compared with the case of formation of positive ions. The probability of formation of negative ions versus the positive ions is 10^{-3} to 1, in an electron-impact type ion source.[6)] In the spark discharge type ion source, the probability appears to be close to this value.

In the present experiment, the following testing materials were used: (1) elementary materials in the form of solid metals or powdered metals, (2) gases, (3) oxide compounds, (4) inter-elementary compounds such as GaAs or LiF, (5) other types of compounds, including almost all of the elements in A-subgroups (typical elements) on the periodic table, except for Po, At, Fr, and Ra.

In this report, the ionic species of polyatomic negative ions detected in the experiment are described, along with some polyatomic positive ions. The negative ions are classified into the following five types: (1) "polymer" negative ions, (2) hydride negative ions, (3) oxide negative ions, (4) carbide negative ions, and (5) other types of negative ions.

Electron affinity of molecules is important to the understanding of molecular phenomena. Reported values of electron affinities are available for some molecules in the literature;[7,57)] however, the experimental determination and theoretical calculation both present great difficulties. The results given here present experimental evidence that molecular ions detected here have positive electron affinity values. The results are discussed with reference to the reported values of electron affinities.[32–56)]

The results are also compared with those obtained from negative ion formation by means of the spark discharge, electron impact, surface ionization, and other methods.

Experimental

Apparatus. The instrument used was a Mattauch-Herzog type double focusing mass spectrograph, equipped with an r f spark discharge type ion source (Mitsubishi Denki Electric Co. Ltd.). Since details of the instrumentation were reported elsewhere,[8–10)] only the operationing conditions are given here: spark voltage 20 kV, pulse width 200 μs, repetition rate 100 s^{-1}, ion accelerating voltage 15 kV for positive and negative ions.

Materials. Sample materials studied are (1) elementary materials in the form of solid metals or powdered metals, (2) gases, (3) oxide compounds, (4) binary compounds such as GaAs or LiF, (5) other types of compounds. They are listed in Table 1.

When the samples are solid materials, the discharge electrodes of the ion source, about 1 $mm^2 \times 5$ mm, are made from them. In this case, it is convenient to maintain a discharge between the electrodes, and to have a long exposure time. When the samples are fine powders, they are packed inside a small (≈1 mm diameter) metal tube, made of gold or nickel, and a platinum counterelectrode is applied. When they are electrical insulators, some oxides for instance, powdered materials are mixed well with pure aluminium powder of equal weight, and pressed[11)] to form rigid electrodes. Some insulators, lithium fluoride crystal for instance, can be ionized with a platinum counterelectrode.

When the samples are gaseous materials, they are introduced into the region of the spark discharge of Pt/Pt electrodes through a capillary leak. In "A/B spark discharge," A and B mean the electrode materials in the spark discharge ion source. This notation will be used throughout this report.

Vacuum discharge ionization is difficult to maintain when the melting point of the electrode is low. Gallium, for instance, is ionized using a gallium arsenide crystal.

† Present address: Oyama Technical College, Nakakuki, Oyama, Tochigi 323.

Table 1. Sample materials for the polyatomic negative ions

Group	Element	Sample materials	Group	Element	Sample materials
IA	H	Hydrogen gas		Ge	Germanium, Crystal
	Li	Lithium fluoride, Crystal			Germanium dioxide, Powder
		Lithium carbonate, Powder		Sn	Tin metal
	Na	Sodium chloride, Crystal			Tin(IV) oxide
		Sodium carbonate, Powder		Pb	Lead metal
	K	Potassium bromide, Crystal	VA	N, P	Ammonium hydrogenphosphate, Powder
		Potassium chloride, Crystal		N	^{15}N-Ammonium sulfate, Powder
		Potassium carbonate, Powder		As	Gallium arsenide, Crystal
	Rb	Rubidium chloride, Crystal			Diarsenic trioxide, Power
		Rubidium chloride, Powder		Sb	Indium antimonide, Crystal
	Cs	Caesium bromide, Crystal			Diantimony trioxide, Powder
		Caesium nitrite, Powder		Bi	Dibismuth trioxide, Powder
IIA	Be	Beryllium, Flake	VIA	O	Metal oxides, Powder
		Beryllium oxide, Powder			Air, Gas
	Mg	Magnesium		S	Cadmium sulfide, Crystal
		Magnesium oxide, Powder			Barium sulfide
	Ca	Calcium, Metal		Se	Zinc selenide, Crystal
		Calcium fluoride, Powder			Selenium dioxide, Powder
	Sr	Strontium carbonate, Powder		Te	Tellurium
	Ba	Barium sulfide			Cadmium telluride, Crystal
		Barium carbonate, Powder	VIIA	F	Lithium fluoride, Crystal
IIIA	B	Boron, Powder			Calcium fluoride, Powder
		Diboron trioxide		Cl	Sodium chloride, Crystal
	Al	Aluminium, Wire			Potassium chloride, Crystal
		Aluminium, Powder			Rubidium chloride, Crystal
	Ga	Gallium arsenide, Crystal			Ammonium chloride, Powder
	In	Indium antimonide, Crystal		Br	Potassium bromide, Crystal
	Tl	Dithallium trioxide, Powder			Caesium bromide, Crystal
IVA	C	Graphite			Silver bromide, Powder
	Si	Silicon, Crystal		I	Ammonium iodide, Powder
		Silicon, Powder			

Results and Discussion

Method and procedure for the assignment of the mass spectral peaks obtained by the spark ion source mass spectroscopy are essentially the same as the experiment of the atomic negative ions.[2)]

Experimental results for the polyatomic negative ions are tabulated in Table 2, along with the experimental results for atomic negative ions[2)] and for polyatomic positive ions which were detected in the positive ion spark source mass spectra using the same samples.

Reported values of electron affinities of the molecules available in the literature[7)] are tabulated in Table 3. In this table, the experimental or theoretical method used to determine the values of electron affinities are given in parentheses by an abbreviation.

Group IA Elements. By spark discharge of Pt/Pt electrodes in an atmosphere of H_2 gas, H^-, H_2^+, H_3^+ ions are detected, but H_2^- ion can not be detected. For the molecular ion of hydrogen, there are many reports in the literature. H_3^+ ion was detected by the parabola-type mass spectrograph, but H_2^- ion could not be detected.[12)] The reported value of the electron affinity of H_2^- ion by the calculation is negative,[50,51)] although H_2^- ion was detected by charge exchange of H_2^+ ion with H_2 gas,[13)] and in a duoplasmatron ion source.[14)] H_3^+, H_5^+, and H_5O^+ ions were detected by glow discharge.[15)]

For the experiment of alkali-metal elements, alkali halide crystals are used as spark discharge electrodes. The polyatomic negative ions of $RbCl^-$, and the polyatomic positive ions of Li_2^+ and LiF^+ are detected in the spark discharge of LiF(crystal)/Pt electrodes.

For the polyatomic ions of alkali-metal elements, there are reports in the literature: MX^-, and MX_2^- ions (M=Li, Na, K, Rb, Cs; X=F, Cl, Br, I) are formed by surface ionization,[16)] LiH_2^- ion by Penning discharge,[17)] $LiCl^+$, $NaCl^+$, Na_2Cl^+, $Na_2Cl_2^+$, KCl^+, and $LiBH_2^+$ by spark discharge.[18)]

Group IIA Elements. In the present experiment, only the Be^- ion is detected for negative ions. No polyatomic negative and positive ions are detected. The positives ions Be^+—Be_{25}^+, $Be_p(BeO)_q^+$,[19)] and Mg^+—Mg_5^+ [4)] are reported to form by spark discharge.

Group IIIA Elements. In this group, many polyatomic negative ions are detected. For the element Al, "polymer" negative ions of Al_2^-—Al_{13}^- are detected by Al/Al spark discharge. The results of detection of Al_2^-—Al_7^- and their relative intensities were already reported.[20)] In addition to these ions, oxide negative ions AlO^-, and AlO_2^- are also detected.

TABLE 2. POLYATOMIC NEGATIVE IONS AND POSITIVE IONS

Group	Element	Atomic	Polyatomic negative ions	Polyatomic positive ions
IA	H	D[a]		H_2^+, H_3^+
	Li	D		Li_2^+, LiF^+
	Na	D		
	K	D		
	Rb	D	$RbCl^-$	
	Cs	D		
IIA	Be	D		
	Mg	(ND)		
	Ca	ND[b]		
	Sr	ND		
	Ba	ND		
IIIA	B	D		
	Al	D	Al_2^-—Al_{13}^-; AlO^-, AlO_2^-	Al_2^+
	Ga	D	Ga_2^-; GaO^-, GaO_2^-; $GaAs^-$, $GaAsH^-$	Ga_2^+
	In	D		
	Tl	D	TlO^-; TlC^-	
IVA	C	D	C_2^-—C_{15}^-; CH^-—$C_{13}H^-$	C_2^+—C_{15}^+
	Si	D	Si_2^-; SiC^-,	Si_2^+—Si_4^+

Group	Element	Atomic	Polyatomic negative ions	Polyatomic positive ions
			SiC_2^-	
	Ge	D	Ge_2^-—Ge_4^-; GeC^-, GeC_2^-	Ge_2^+—Ge_4^+
	Sn	D	SnC^-, SnC_2^-	
	Pb	D	PbC^-	
VA	N	ND		
	P	D	PO^-—PO_4^-	
	As	D	As_2^-; AsO^-; AsH^-, As_2H^-; AsC^-—AsC_3^-	As_2^+, AsH^+
	Sb	D	Sb_2^-	
	Bi	D		
VIA	O	D	O_2^-; OH^-, O_2H^-	O_2^+
	S	D	S_2^-, S_3^-	S_2^+
	Se	D	Se_2^-—Se_4^-	Se_2^+
	Te	D	Te_2^-	
VIIA	F	D		F_2^+; FH^+; LiF^+
	Cl	D	Cl_2^-; $RbCl^-$	
	Br	D	Br_2^-, Br_3^-; BrH^-; Br_2O^-	Br_2^+; BrH^+; Br_2O^+, $Br_2O_2^+$
	I	D		

a) Detected. b) Not detected.

TABLE 3. REPORTED VALUES OF THE ELECTRON AFFINITIES OF THE MOLECULES (—: No data are available in the literature)

Element	Present study	Electron affinity values/eV
Rb	$RbCl^-$	—
Al	Al_2^-—Al_{13}^-	—
	AlO^-	3.68 ± 0.13(SI, 32), 2.60(AA, 33)
	AlO_2^-	4.11 ± 0.13(SI, 32)
Ga	Ga_2^-	—
	GaO^-	—
	GaO_2^-	—
Tl	TlO^-	—
	TlC^-	—
C	C_2^-	$\leqslant3.54\pm0.05$(P, 34), 4.0(SI, 35), $>2.9\pm0.5$(DEC, 36)
	C_3^-	2.5(SI, 35)
	CH^-	0.74 ± 0.05(P, 34), $\geqslant4.1\pm0.4$(DEC, 36)
	C_2H^-	$\leqslant3.73\pm0.05$(P, 34), $>2.3\pm0.7$(DEC, 36)
	C_4^-—C_{15}^-	—
	C_3H^-—$C_{13}H^-$	—
Si	Si_2^-	—
	SiC^-	—
	SiC_2^-	—
Ge	Ge_2^-—Ge_4^-	—
Sn	SnC^-	—
	SnC_2^-	—
Pb	PbC^-	—

Element	Present study	Electron affinity values/eV
P	PO^-	$\leqslant1.13$(HF, 37)
	PO_2^-—PO_4^-	—
As	As_2^-	—
	AsO^-	—
	AsH^-	—
	As_2H^-	—
	AsC^-—AsC_3^-	—
Sb	Sb_2^-	>0(OBS, 38)
O	O_2^-	0.440 ± 0.008(PE, 39), 0.5 ± 0.1(CE, 40), $\geqslant0.48$(CE, 41), 0.42(DE, 42), 0.15 ± 0.05(P, 43)
	OH^-	1.91 ± 0.10(HF, 44)
	O_2H^-	4.6(BH, 45)
S	S_2^-	>2.0(ATT, 46)
	S_3^-	—
Se	Se_2^-—Se_4^-	>0(OBS, 38)
Te	Te_2^-	>0(OBS, 38)
Cl	Cl_2^-	2.45 ± 0.15(CE, 40), 2.46 ± 0.14(CE, 47), <1.7(ATT, 48)
	$RbCl^-$	—
Br	Br_2^-	2.55 ± 0.10(CE, 40), >0(OBS, 49), 2.51 ± 0.10(CE, 58)
	Br_3^-	—
	BrH^-	—
	Br_2O^-	—

SI: Surface ionization. AA: Constituent atom electron affinity(dissociation energy). P: Incoherent photon detachment. DEC: Electron impact with analytic deconvolution. HF: Hartree-Fock calculation. OBS: Observation in mass spectrum. PE: Photoelectron spectroscopy with fixed frequency. CE: Charge exchange. DE: Dissociation energy. BH: Born-Haber cycle calculation. ATT: Dissociative electron attachment.
(Numbers in the parentheses are reference numbers.)

Table 4. "Polymer" negative ions

Group	IA	IIA	IIIA		IVA			VA		VIA				VIIA	
Element	Li	Be	Al	Ga	C	Si	Ge	As	Sb	O	S	Se	Te	Cl	Br
M^-	D	D	D	D	D	D	D	D	D	D	D	D	D	D	D
M_2^-		D	D	D	D	D	D	D	D	D	D	D	D	D	D
M_3^-			D		D		D				D	D			D
M_4^-			D		D		D					D			
⋮			⋮		⋮										
M_{13}^-			D		⋮										
⋮					⋮										
M_{15}^-					D										

For the element Ga, the diatomic negative ion Ga_2^- and the oxide negative ions GaO^- and GaO_2^- are detected by spark discharge of GaAs/GaAs. In this experiment, $GaAs^-$ and $GaAsH^-$ ions are also detected. For the element Tl, TlO^-, and TlC^- ions are detected.

For polyatomic positive ions of these elements, Al_2^+ and Ga_2^+ ions are detected; these results were already reported.[20]

Al_2^+—Al_{14}^+ ions were reported to form by spark discharge,[19] and BO^- and BO_2^- ions are reported to form by surface ionization.[21] Electron affinity values are available for AlO^- (2.60, 3.68 eV) and AlO_2^- (4.11 eV) (Table 3).

Group IVA Elements. In this group, many polyatomic negative ions are detected. For the element C, "polymer" negative ions C_2^-—C_{15}^-, and hydride negative ions CH^-—$C_{13}H^-$ are detected. For Si: Si_2^- and SiC^- and SiC_2^- ions are detected; for Ge: Ge_2^-, Ge_3^- and Ge_4^-; GeC^- and GeC_2^- ions; for Sn: SnC^- and SnC_2^- ions; and for Pb: PbC^- ions. The following positive ions are detected in these elements: C_2^+—C_{15}^+; Si_2^+—Si_4^+. Ge_2^+—Ge_4^+ "polymer" positive ions are also detected.

In the literature,[22,23] CS^-, CS_2^-, OCN^-, SCN^- ions are reported to form by ion-molecule reactions. SiO_2^- ions are reported by surface ionization.[24] Several positive "polymer" ions of C, C_2^+—C_{31}^+, are reported to form by spark discharge.[18,25,26,27]

The electron affinity values are available for the molecules C_2^-(2.9—4.0 eV), CH^-(0.74—4.1 eV), C_2H^-(2.3—3.73 eV) (Table 3).

Group VA Elements. In this group, for the element N, no atomic negative ion was detected,[2] and no polyatomic negative ion was detected. For the element P: PO^-, PO_2^-, PO_3^-, and PO_4^- are detected. For the element As: As_2^-; AsH^-, and As_2H^-; AsO^-; AsC^-, AsC_2^-, and AsC_3^- ions are detected. For the element Sb: Sb_2^- ion is detected. For the polyatomic positive ions of this group, As_2^+ and AsH^+ ions are detected.

The literature reports PH^- and PH_2^-, AsH^- and AsH_2^- ions by electron impact,[28] and N_3^-, CN^-, $C_2N_3^-$, C_3NO^-, $C_2N_4^-$, $C_2N_6^-$, $C_3N_2O^-$, $C_2N_5^-$, *etc.* ions by glow discharge.[29]

The electron affinity values are available for the molecules PO^- (<1.13 eV), and Sb_2^- (>0 eV) (Table 3).

Group VIA Elements. For the element O: O_2^-, O_2H^- and OH^- negative ions are detected. For the element S: S_2^- and S_3^-; for Se: Se_2^-, Se_3^-, and Se_4^-; and for Te, Te_2^-. These "polymer" negative ions are detected by the spark discharges of CdS(crystal)/Pt, CdSe(crystal)/Pt, and CdTe(crystal)/Pt, respectively. Positive ions of O_2^+, S_2^+, and Se_2^+ are also detected.

The literature reports O_3^-, OH^-, NO_2^-, SO_2^-, CS^-, CS_2^-, S_n^- (n=2—6) ions,[22] SF_6^-,[30] SCN^-, OCN^-, HS^-, NH_2S^- ions,[23] and S_{12}^+ ion.[31]

Electron affinity values are available for the molecules O_2^- (0.15—0.5 eV), OH^- (1.825—1.91 eV), O_2H^- (4.6 eV), S_2^- (2.0 eV), Se_n^- (n=2—4: >0 eV), and Te_2^- (>0 eV) (Table 3).

Group VIIA Elements. For Cl, Cl_2^-, and $RbCl^-$ ions are detected by spark discharge of RbCl/Pt. For Br, Br_2^-, Br_3^-, BrH^-, and Br_2O^- ions are detected

Table 5. Hydride negative ions

Group	IVA	VA	VIA	VIIA	
Element	C	As	O	Cl	Br
M^-	D	D	D	D	D
MH^-	D	D	D		D
MH_2^-	D	D	—		
M_2H^-	D	D	D		

Table 6. Oxide negative ions

Group	IA	IIIA			VA		VIIA
Element	H	Al	Ga	Tl	P	As	Br
M^-	D	D	D	D	D	D	D
MO^-	D	D	D	D	D	D	—
MO_2^-	D	D	D		D		—
MO_3^-					D		—
MO_4^-					D		—
M_2O^-							D

Table 7. Carbide negative ions

Group	IVA				VA	
Element	Si	Ge	Sn	Pb	As	Sb
M^-	D	D	D	D	D	D
MC^-	D	D	D	D	D	D
MC_2^-	D	D	D		D	D
MC_3^-					D	

Table 8. "Polymer" positive ions

Group	IA		IIIA		IVA			VA	VIA			VIIA	
Element	H	Li	Al	Ga	C	Si	Ge	As	O	S	Se	F	Br
M_2^+	D	D	D	D	D	D	D	D	D	D	D	D	D
M_3^+	D				D	D	D			D			
M_4^+					D	D	D						
⋮					⋮								
M_{15}^+					D								

Table 9. Hydride positive ions

Group	VA	VIIA	
Element	As	F	Br
MH^+	D	D	D
M_2H		D	

Table 10. Oxide positive ions

Group Element	VIIA Br
M_2O^+	D
$M_2O_2^+$	D

Table 11. Other types of positive ions

LiF^+	Li_2F^+

by AgBr/Pt spark discharge. Some polyatomic positive ions of the elements in this group are found: F_2^+, F_2H^+, and LiF^+ ions for the element F, and Br_2^+, Br_2O^+, $Br_2O_2^+$, and BrH^+ ions for the element Br. These are detected by the spark discharge of LiF/Pt and AgBr/Pt, respectively.

Electron affinity values are available for the molecules Cl_2^- (1.7—2.46 eV) and Br_2^- (>0—2.55 eV) (Table 3).

In summary, we have described the ionic species of polyatomic negative ions formed by the spark discharge type ion source for the elements in A-subgroups on the periodic table, along with the polyatomic positive ions. For the molecules that are detected as negative ions in this experiment, the reported values of the electron affinities are all positive. For the molecules having negative electron affinity values, available in the literature: (H_2^-: <0 eV,[50] −2.85 eV;[51] CO^-: −1.8 eV;[52] CO_2^-: >−0.9 eV;[53] N_2^-: −1.6 eV,[54] −11.345 eV;[55] HF^-: <0 eV[56]); no polyatomic negative ions can be detected in this experiment. Therefore, it seems that the electron affinity values are positive for the molecules which are detected as negative ions in this experiment, although there are many examples that the molecules can not be detected as negative ions in spite of the positive electron affinity values of them. This conclusion is in line with the case of atomic negative ions.[2] If this assumption is correct, the experimental results described in this report give experimental evidence that the ionic species that are detected as negative ions have the positive electron affinity values.

The polyatomic negative ions described in this report are classified into the following four types: (1) "polymer" negative ions, (2) hydride negative ions, (3) oxide negative ions, and (4) carbide negative ions. They are tabulated in Tables 4—7. Polyatomic positive ions detected can also be classified into the following four types: (1) "polymer" positive ions, (2) hydride positive ions, (3) oxide positive ions, and (4) other types of positive ions. They are tabulated in Tables 8—11. These tables indicate the following features for the formation of the polyatomic negative and positive ions by the spark discharge type ion source in the elements of A-subgroups on the periodic table.

(1) In the elements for which atomic negative ions can not be detected, no polyatomic negative ions can be detected.

(2) The elements, whose negative and positive "polymer" ions can easily be detected are identical, except for the elements H, Be, Sb, F, and Cl. They belong mostly to the IIIA, IVA, VA, VIA groups in the periodic table.

(3) Few hydride positive ions are detected, compared to the number of hydride negative ions; these are observed for the elements C, As, O, Cl, Br.

(4) Oxide negative ions are observed for the elements H, Al, Ga, Tl, P, As, and Br, whereas oxide positive ions are observed only for the element Br.

(5) Carbide negative ions are observed for the elements Si, Ge, Sn, Pb, As, and Sb. No carbide positive ions can be detected in this experiment.

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References

1) Part II: H. Kishi, *Bull. Chem. Soc. Jpn.*, **54**, 703 (1981).
2) T. Makita, H. Kishi, and K. Kodera, *Mass Spectroscopy (Japan)*, **21**, 293 (1973).
3) J. Mattauch and R. Herzog, *Z. Phys.*, **89**, 786 (1934).
4) H. Hintenberger, J. Franzen, and K. D. Schuy, *Z. Naturforsch., Teil A*, **18**, 1236 (1963).
5) K. D. Schuy, J. Franzen, and H. Hintenberger, *Z. Naturforsch., Teil A*, **19**, 153 (1964).
6) C. E. Melton, "Mass Spectrometry of Organic Ions," ed by F. W. McLafferty, Academic Press (1963), p. 163.
7) H. R. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, "Energetics of Gaseous Ions," National Bureau of Standards, Washington, D. C., 20234 (1977).
8) N. Sasaki and J. Kai, *Mass Spectroscopy (Japan)*, **7**, 64 (1959).

9) M. Gotoh and J. Kai, *Mitsubishi Denki Lab. Report*, **1**, 51 (1960).
10) T. Makita and K. Kodera, *Mass Spectroscopy (Japan)*, **12**, 1 (1964).
11) F. Konishi, *Mass Spectroscopy (Japan)*, **16**, 251 (1968).
12) J. W. Hiby, *Ann. Phys.*, **34**, 473 (1939).
13) V. I. Khvostenko and V. M. Dukelsky, *Soviet Phys. -JETP*, **7**, 709 (1958).
14) E. B. Carter and R. H. Davis, *Rev. Sci. Instrum.*, **34**, 93 (1963).
15) P. H. Dawson and A. W. Tickner, *J. Chem. Phys.*, **37**, 672 (1962).
16) H. Ebinghaus, *Z. Naturforsch.*, *Teil A*, **19**, 727 (1964).
17) H. Baumann, K. Bethge, and E. Heinicke, *Nucl. Instrum. Methods*, **46**, 43 (1967).
18) K. Goshgarian and J. Jensen, ASTM-E14, 12th Annual Meeting, preprint, p. 350, (1964).
19) J. Franzen and H. Hintenberger, *Z. Naturforsch., Teil A*, **16**, 535 (1961).
20) K. Kodera and T. Makita, Twelfth Annual Conference on Mass Spectrometry and Allied Topics, p. 486 (1964).
21) S. Taniguchi, *Mass Spectroscopy (Japan)*, **14**, 139 (1966).
22) J. G. Dillard and J. L. Franklin, *J. Chem. Phys.*, **48**, 2349 (1968).
23) J. G. Dillard and J. L. Franklin, *J. Chem. Phys.*, **48**, 2353 (1968).
24) D. C. Newton, J. Sanders, and A. C. Tyrrell, *Nature*, **187**, 683 (1960).
25) W. L. Baun, F. N. Hodgson, and M. Desgardino, *J. Chem. Phys.*, **38**, 2787 (1963).
26) M. S. Chupakhin, G. G. Glavin, and L. T. Duev, *Zh. Tekh. Fiz.*, **33**, 1281 (1963).
27) K. Dornenberg, H. Hintenberger, and J. Franzen, *Z. Naturforsch.*, *Teil A*, **19**, 532 (1961).
28) H. Ebinghaus, K. Kraus, W. Müller-Duysing, and H. Neuert, *Z. Naturforsch.*, *Teil A*, **19**, 732 (1964).
29) A. N. Hayhurst and P. J. Padley, *Trans. Faraday Soc.*, **63**, 1620 (1967).
30) A. J. Ahearn and N. B. Hannay, *J. Chem. Phys.*, **21**, 119 (1953).
31) J. Buckler, *Angew. Chem., Int. Ed. Engl.*, **5**, 965 (1966).
32) R. D. Srivastava, O. M. Uy, and M. Farber, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1388 (1972).
33) A. F. Gaines and F. M. Page, *Trans. Faraday Soc.*, **62**, 3086 (1966).
34) D. Feldmann, *Z. Naturforsch.*, *Teil A*, **25**, 621 (1970).
35) R. E. Honig, *J. Chem. Phys.*, **22**, 126 (1954).
36) J. C. J. Thyne and K. A. G. MacNeil, *J. Phys. Chem.*, **75**, 2584 (1971).
37) D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967).
38) V. M. Dukelskii and N. I. Ionov, *Dokl. Akad. Nauk SSSR*, **81**, 767 (1951).
39) R. J. Cellotta, R. A. Bennett, J. L. Hall, M. W. Siegel, and J. Levine, *Phys. Rev. A*, **6**, 631 (1972).
40) A. P. M. Baede, *Physica*, **59**, 541 (1972).
41) J. Berkowitz, W. A. Chupka, and D. Gutman, *J. Chem. Phys.*, **55**, 2733 (1971).
42) W. T. Zemke, G. Das, and A. C. Wahl, *Chem. Phys. Lett.*, **14**, 310 (1972).
43) S. Burch, S. J. Smith, and L. M. Branscomb, *Phys. Rev.*, **112**, 171 (1958).
44) P. E. Cade, *J. Chem. Phys.*, **47**, 2390 (1967).
45) J. Weiss, *Trans. Faraday Soc.*, **31**, 966 (1935).
46) K. Jäger and A. Henglein, *Z. Naturforsch.*, *Teil A*, **21**, 1251 (1966).
47) D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *Chem. Phys. Lett.*, **15**, 257 (1972).
48) R. F. Baker and J. T. Tate, *Phys. Rev.*, **53**, 683 (1938).
49) J. P. Blewett, *Phys. Rev.*, **49**, 900 (1936).
50) T. E. Sharp, Lockheed Report LMSC 5-10-69-9 (1969).
51) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).
52) R. D. Rempt, *Phys. Rev. Lett.*, **22**, 1034 (1969).
53) J. N. Bardsley, *J. Chem. Phys.*, **51**. 3384 (1969).
54) F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer*, **5**, 369 (1965).
55) J. Comer and F. H. Read, *J. Phys. B*, **4**, 1055 (1971).
56) V. Bondybey, P. K. Pearson, and H. F. Schaefer, *J. Chem. Phys.*, **57**, 1123 (1972).
57) Sir Harrie Massey, "Negative Ions, Third Edition," Cambridge University Press (1976).
58) W. A. Chupka, J. Berkowitz, and D. Gutman, *J. Chem. Phys.*, **55**, 2724 (1971).