An Overlooked Series of Gas Phase Diatomic Metal Oxide Ions that Are Long-lived[†]

Keith Schofield*

Materials Research Laboratory, University of California, Santa Barbara, California 93106-5121

Received: November 7, 2005; In Final Form: December 20, 2005

Although the "Golden" years of spectroscopy and the major studies on ionization processes now are behind us, as with many branches of science, much yet remains to be gleaned from such topics that is both full of interest and of significance to present day research. Presented here is one such overlooked example, an observation that relates to both these fields. An analysis is presented for the periodic table concerning the gas-phase thermochemical nature of MO^+ and MO_2^+ ions. Unexpectedly, a pattern of 18 elements has been identified that exhibit the potential for having long-lived MO^+ ions. Normally such molecular ions are expected to decay extremely rapidly by dissociative recombination with electrons, but in particular, 12 of this group behave not like molecules but rather as atomic ions. These are the diatomic oxide ions of Sc, Y, La, Zr, Hf, Ce, Pr, Nd, Pm, Gd, Tb, and Th. In the gas phase, they decay by much slower three-body recombination channels. As may be noted, these elements are located in the first two columns of the transition elements, among the earlier rare earths and an actinide. From all the elements, UO_2^+ is the only dioxide ion that behaves similarly. These findings now elevate the potential importance of these ions and should facilitate their spectral characterization. Moreover, subsequent comparisons with spectra of well-known isoelectronic and isovalent neutral monoxides and other diatomics will help in the stimulation of further theoretical advances. In addition, once characterized, an ease of spectrally monitoring such ionic states will provide a useful analytical tool.

I. Introduction

The term chemiluminescence to describe spectral emission arising from chemical processes is a very old term and was being discussed in the literature a century ago in both the physical and biological sciences.[1] However, the expression chemi-ionization began to appear just over 50 years ago and may possibly be attributed to Behrens.[2] He suggested that the reverse of the dissociative recombination of ions with electrons, namely

$$AB^+ + e^- = A + B$$

being suggested then as an ionospheric reaction, might possibly be the source of ions in flames. This was accepted quite rapidly, especially as it came at a time when interest was turning to the closer examination of energy dispersal in chemical reactions. Increasingly, it was obvious that collisional and chemical energy could be retained in the products not only as rotational, vibrational, or electronic excitations but also as ionization, the reaction being stabilized by the shedding of an electron. Over the next several decades, such studies of this energy redistribution opened new vistas with techniques being developed in reaction dynamics, in kinetics, and in the detailed characterizations of spectroscopic emissions. Such research also helped spawn the era of commercial monitoring instrumentation with such equipment as the flame ionization detector for total hydrocarbons,[3−5] and chemiluminescent monitors for NO_x, ozone, and total sulfur or phosphorus.[6] More importantly, it introduced more rigorously the concept of nonequilibrium distributions and new nonthermal methods for the production of radiation or electron plasmas at lower temperatures. A book dedicated to gas-phase chemiluminescence and chemi-ionization appeared in 1985[7] but as seen therein still showed few examples of chemi-ionization.

It was soon apparent that chemi-ionization was restricted to a much narrower subset of reactions than chemiluminesence. It requires more energy and obviously needs reactions that involve very strong bond formation. Additionally, the product cannot generally be larger than a di- or triatomic to ensure the required specificity of the channeling of the energy. As a result, most chemi-ionization processes involve oxide-, hydroxide-, or halide-forming bonds. The majority involve oxides. In addition, external energy must also be provided in the majority of cases studied to make up for the oft-observed deficit. Typifying cases are in shock-heated air. At high temperatures in air it is well known that the electrons are produced by chemi-ionization that produces ions such as NO^+, N_2^+, and O_2^+ by reactions of the type

$$N + O = NO^+ + e^- \quad \Delta H_0{}^\circ = +267.07 \pm 0.02 \text{ kJ mol}^{-1}$$

These ions are also present in the earth's ionosphere but are produced there by more direct-ionization and charge-transfer reactions. As can be seen though from the reaction energetics, any such ion is prone to dissociative recombination with electrons via the exothermic reverse channel. Such dissociative recombination kinetic processes have been studied extensively and shown to be universally very rapid.[8−10] Consequently, chemi-ionization has long been known as a possible method for producing electron plasmas, but these have the reputation of being short lived. The minute the excitation energy is removed so are the electrons and the ions.

It was in this regard, almost thirty years ago, that the author was involved with programs to create electron plasmas chemically. During that work a specific class of reactions became

---

[†] Part of the special issue "David M. Golden Festschrift".

* To whom correspondence should be addressed. Phone: (805) 681-0916. Fax (805) 965-9953. E-mail: combust@mrl.ucsb.edu.

10.1021/jp0564187 CCC: $33.50

TABLE 1: Enthalpy Values for Reactions 1 and 6[a]

$M + O_2 = MO + O$ (1), ΔH_0^o kJ mol^{-1} (UpperValue)

$M^+ + O_2 = M^+O + O$ (6) (LowerValue)

+68 H +12																	+494 He -567
+158 Li +409	+59 Be +104											-314 B +126	-578 C -313	-133 N -642	0 O -149	+278 F -171	+494 Ne -285
+246 Na +435	+247 Mg +272											-15 Al +343	-299 Si +32	-97 P -301	-22 S -29	+228 Cl +27	+491 Ar +225
+218 K +465	+99 Ca +161	-174 Sc -195	-175 Ti -169	-129 V -81	+37 Cr +137	+141 Mn +212	+90 Fe +154	+122 Co +181	+121 Ni +228	+219 Cu +381	+337 Zn +334	+124 Ga +432	-163 Ge +163	+17 As -68	+68 Se +72	+263 Br +133	+493 Kr +282
+221 Rb +464	+89 Sr +198	-216 Y -215	-272 Zr -255	-233 Nb -206	-31 Mo +4	-20 Tc	-24 Ru +104	+54 Rh +231	+259 Pd +353	+278 Ag +375	+262 Cd	+194 In +456	-31 Sn +186	+70 Sb +11	+136 Te +108	+262 I +192	+425 Xe
+212 Cs +436	-54 Ba +100	-303 La* -364	-303 Hf -233	-301 Ta -300	-174 W -151	-98 Re +67	-77 Os +35	+83 Ir +144	+108 Pt +194	+275 Au	+476 Hg	+234 Tl	+122 Pb +285	+160 Bi +277	Po	At	Rn
Fr	Ra	-300 Ac†															
		*	-296 Ce -358	-253 Pr -309	-203 Nd -254	-136 Pm -169	-68 Sm -77	+12 Eu +82	-214 Gd -253	-226 Tb -250	-108 Dy -95	-109 Ho -92	-115 Er -97	-4 Tm +20	+80 Yb +109	-179 Lu -56	
		†	-380 Th -351	-294 Pa	-261 U -269	-242 Np -258											

[a] In the cases of N, F, He, Ne, Ar, and Kr in these tables, the ion is MO^+.

apparent from trends in the periodic table. Specific metal reactions were identified that could produce very stable long-lived chemi-ions that were not prone to such dissociative recombination. Despite the passing years, the nature of these reactions especially in relation to their pattern in the periodic table still appears to remain unrealized. These findings were published originally in two now obscure and probably no longer traceable reports[11,12] but still are not known generally. These potentially very useful reactions that produce diatomic metal oxide ions are described herein in detail. Modern techniques now can readily begin to examine their previously unknown spectroscopy and better establish their chemical thermodynamic properties. It also introduces new possibilities to monitor their energy distributions in plasmas and examine theoretically the detailed role of the structural configurational effects in these elements.

For this analysis, the necessary chemical thermodynamic data, namely, the ionization potentials of all the elements and their mono- and dioxides, together with the bond strengths of the mono- and dioxides, have been critically evaluated. Their values in many cases now are beginning to be more reliably established and are seen to be sufficiently accurate for this analysis. Original source data have been used throughout to produce a reliable set of recommended thermochemical values. These are to be published elsewhere in the foreseeable future as a reference data set and to a large extent will be the same values listed and used herein. Any future slight changes that may occur in these databases will have no particular affect on the conclusions and observations reported herein.

II. Chemiluminescence

A very common class of chemiluminescent reactions is that of the elements with molecular oxygen, namely, reaction 1

$$M + O_2 = MO + O \quad \Delta H = -D(MO) + D(O_2) \qquad (1)$$

As indicated by the reaction enthalpy, the available energy arises from the difference between the dissociation bond strengths of the metal oxide and molecular oxygen. The bond strength of oxygen is 493.6 ± 0.1 kJ mol^{-1} at absolute zero. Consequently, as seen in Table 1, this is not a particularly restrictive value and reaction 1 is exothermic for almost half of the periodic table and not too endothermic for numerous more. The enthalpy error bars are slight, reflecting those of D(MO). As a result, using this as a spectral source, with or without additional energy it has been possible to characterize the spectral systems of many oxides. To this day this continues, with oxygen or other oxidants such as NO_2, N_2O, O_3, or SO_2. Recent papers, for example, examine the detailed electronic systems of MnO[13] and YO.[14] This reaction was even used in earlier times as a measure of the lower limits of the oxide bond strengths. For example, values were estimated for the dissociation energies of EuO and SmO from the short wavelength cut off in their chemiluminescent spectra.[15]

III. Chemi-Ionization

As indicated above, and is quite logically obvious, chemi-ionization requires more energy if excitation is to the ionized state. In oxygen systems, two such reactions are plausible, reactions 2 and 3.

$$M + O = M^+O + e^- \quad \Delta H = -D(MO) + IP(MO) \qquad (2)$$
$$= -D(M^+O) + IP(M)$$

$$M + O_2 = MO_2{}^+ + e^- \quad \Delta H = -D(MO) - D(MO{-}O) + IP(MO_2) + D(O_2) \qquad (3)$$
$$= -D(M^+O) - D(M^+O{-}O) + IP(M) + D(O_2)$$

The energetics of these reactions can be expressed either in terms of ionization potentials of the oxides or the dissociation energies of their oxide ions. In these formulations, D is the dissociation energy of the specific bond indicated. IP is the ionization potential or ionizing energy of the respective element or oxide to its corresponding undissociated and ground-state ion. $D(M^+O)$ implies dissociation to $M^+ + O$. As seen in Table 2, in the cases of He, Ne, Ar, Kr, N, F, these have a higher ionization potential than O, which implies the lower energy channel is to $M + O^+$, that is $D(MO^+)$. $D(MO_2{}^+)$ refers to dissociation to the diatomic oxide ion and atomic oxygen products.

TABLE 2: Enthalpy Values at 0 K for the Ionization of the Gaseous Elements and Their Diatomic Oxides

$M = M^+ + e^-$ IP(M), Upper Value, kJ mol^{-1}

$MO = (MO)^+ + e^-$ IP(MO), Lower Value

1312 H 1256																	2372 He 1311
520 Li 825	900 Be 945											801 B 1240	1086 C 1352	1402 N 894	1314 O 1165	1681 F 1232	2081 Ne 1302
496 Na 685	738 Mg 773											578 Al 936	787 Si 1118	1012 P 809	1000 S 993	1251 Cl 1050	1521 Ar 1251
419 K 666	590 Ca 656	633 Sc 612	659 Ti 658	651 V 700	653 Cr 757	717 Mn 788	762 Fe 826	760 Co 820	737 Ni 845	745 Cu 908	906 Zn 903	579 Ga 888	762 Ge 1088	944 As 859	941 Se 946	1140 Br 1010	1351 Kr 1140
403 Rb 646	549 Sr 666	600 Y 590	640 Zr 657	652 Nb 690	684 Mo 719	702 Tc	710 Ru 839	720 Rh 897	804 Pd 898	731 Ag 828	868 Cd	558 In 820	709 Sn 926	831 Sb 772	869 Te 841	1008 I 939	1170 Xe
376 Cs 600	503 Ba 656	538 La* 478	659 Hf 728	728 Ta 762	759 W 782	756 Re 921	814 Os 926	865 Ir 926	864 Pt 950	890 Au	1007 Hg	589 Tl	716 Pb 878	703 Bi 820	812 Po	At	1037 Rn
393 Fr	509 Ra	499 Ac†															
			*	534 Ce 473	528 Pr 473	533 Nd 482	539 Pm 507	545 Sm 535	547 Eu 618	593 Gd 555	566 Tb 542	573 Dy 587	581 Ho 598	589 Er 608	597 Tm 621	603 Yb 632	524 Lu 646
			†	609 Th 637	568 Pa	598 U 582	605 Np 589										

TABLE 3: Enthalpy Values for the Chemi-Ionization Reactions 2 and 3 Producing M^+O and MO_2^+ Ions

$M + O = M^+O + e^-$ (2), ΔH_0^o kJ mol^{-1} (UpperValue)

$M + O_2 = MO_2^+ + e^-$ (3) (LowerValue)

+830 H +896																	+1311 He
+489 Li	+510 Be											+433 B +374	+280 C +225	+267 N +491	+671 O +1097	+1016 F +1166	+1301 Ne
+437 Na +442	+520 Mg +740											+427 Al +642	+325 Si +406	+218 P +489	+477 S +622	+785 Cl +979	+1251 Ar
+390 K +380	+260 Ca +338	-56 Sc +272	-5 Ti +145	+77 V +240	+300 Cr +493	+435 Mn +643	+423 Fe +563	+448 Co	+472 Ni	+633 Cu +675	+746 Zn	+518 Ga	+431 Ge	+383 As	+520 Se +791	+779 Br +1046	+1139 Kr +1625
+373 Rb	+261 Sr +326	-109 Y +203	-109 Zr -14	-36 Nb -93	+194 Mo +193	Tc	+321 Ru +484	+457 Rh +617	+664 Pd	+612 Ag	Cd	+520 In	+401 Sn	+348 Sb	+483 Te +823	+707 I	Xe
+318 Cs	+109 Ba +64	-319 La* -15	-69 Hf -38	-33 Ta -116	+114 W +157	+329 Re	+356 Os +369	+515 Ir +548	+564 Pt +695	Au	Hg	Tl	+507 Pb +793	+486 Bi	Po	At	Rn
Fr	Ra	Ac†															
			*	-317 Ce -14	-274 Pr +8	-215 Nd +47	-123 Pm +225	-27 Sm +391	+136 Eu +620	-153 Gd +90	-178 Tb +119	-15 Dy +373	-5 Ho +296	-1 Er +379	+123 Tm +599	+218 Yb +769	-27 Lu +392
			†	-237 Th -222	Pa	-165 U -410	-147 Np -234										

Reaction 2 depends on the relative magnitudes of the oxide bond strength and its ionization potential. Listed in Table 2, the ionization potentials of the diatomic oxides are seen to be uniformly quite large throughout the periodic table. Consequently, if the chemi-ionization reaction 2 is to be exothermic, it will require a strong MO bond formation. LaO and the first few rare earth monoxides are seen to have the lowest oxide ionization potentials in the periodic table being less than the general magnitude and this also facilitates the process for them. The same but even more stringent argument applies to reaction 3 where a larger ionization potential and the loss of energy in breaking the O_2 bond quite often offset the formation energy acquired by the second oxide bond in the ion.

Utilizing the most reliable current chemical thermodynamic values, the energetics of all the elements have been calculated wherever available and are listed in Table 3 for the chemi-ionizing reactions 2 and 3. The enthalpy error bars for reaction 2 relate directly to those in the values of IP(MO) and D(MO) or solely to those of $D(M^+{-}O)$ if this is measured directly. Reaction 3 is more involved, and the accuracy of the enthalpy value is controlled by the combined errors in $IP(MO_2)$ and the two bond strengths of MO_2. Invariably, error bars are much less for reaction 2 than 3.

IV. Long-Lived Diatomic Oxide Ions

A pattern in Table 3 for the energetics of reactions 2 and 3 is apparent and one that has not been reported or exploited previously. Negative values in Table 3 for reactions 2 and 3 imply that these processes are exothermic. Large sections of the periodic table are strongly endothermic. However, exclusive to the first three columns of the transition elements and to many of the rare earth and actinide elements, pronounced exothermicities are noted. The important implication is that, once formed, these ions will be more reluctant to recombine with electrons. Recombination will be as with atomic ions, that is, by much slower three-body reactions such as indicated by reaction 4, where Z represents any collision partner in the system

$$M^+ + e^- + Z = M + Z \tag{4}$$

$$M^+O + e^- + Z = MO + Z$$

Unlike molecular ions in general, these exothermic cases are not vulnerable to rapid dissociative recombination by the reverse of their formation channel. In this manner they are unique. As will be discussed further there may be alternate options for ion transformations between M^+O and MO_2^+, for example, depend-

TABLE 4: Enthalpy Values (kJ mol^{-1}) at 0 K for the Various Thermal Dissociation Channels of Metal Oxides and Their Ions for the First Three Columns of the Transition Elements, the Rare Earths, and Three Actinides

M	$MO = M^+O + e^-$	$M^+O = M^+ + O$	$MO_2 = MO_2^+ + e^-$	$MO_2^+ = M^+O + O$	$MO_2^+ = M^+ + O_2$
Sc	612	689	826	166	361
Y	590	720	819	182	397
La	478	857	783	190	553
Ti	658	664	917	344	514
Zr	657	749	917	399	654
Hf	728	727	902	463	697
V	700	574	939	330	411
Nb	690	700	781	551	757
Ta	762	761	844	577	844
Ce	473	852	946	191	548
Pr	473	802	926	212	520
Nd	482	748	917	232	486
Pm	507	662	936	146	314
Sm	535	571	965	76	154
Eu	618	412	1042	10	−73
Gd	555	747	917	251	503
Tb	542	744	994	197	447
Dy	587	588	1023	106	200
Ho	598	586	1032	193	285
Er	608	590	1042	114	210
Tm	621	473	1052	18	−2
Yb	632	385	1061	−57	−166
Lu	646	550	1177	75	132
Th	637	845	839	479	831
U	582	763	591	739	1008
Np	589	752	611	581	839

ing on which is formed first and which is the more stable of the two in its specific environment. Also, as will be seen, the case of MO_2^+ ions also has alternate channels. But nevertheless, recombination will not occur rapidly particularly in the majority of these specific M^+O ion cases and long-lived ions can be made to exist.

At this point it might be appropriate to define what is meant in this paper by the term long-lived. Approximate rate constants for reaction 4 with atomic ions, M^+, have been reported for the alkali metals, Tl, Ga, In, Pb, Mn, and Cr. These indicate no pronounced sensitivity to atomic number or temperature, and values, expressed as $k[Z]$, are of the order of 3×10^{-8}–2×10^{-9} cm^{-3} molecule^{-1} s^{-1} or less.[16–18] Assuming a value of 10^{-8} implies, for electron levels of order 10^{10} cm^{-3}, that they will have a half-life at atmospheric pressure of about 20 ms. As pressure or the electron levels are decreased below these values the lifetime increases proportionally. Consequently at reduced pressure, these ions can live for a significant fraction of a second. For comparison, an ion such as NO^+ has a rate constant for dissociative recombination with electrons of 4.3×10^{-7} (300 K) to 1.1×10^{-7} (2000 K) cm^{-3} molecule^{-1} s^{-1}.[19] For a similar level of electrons, NO^+ has a lifetime of about 1 ms or less, independent of pressure. Consequently, the lifetimes that result from an alternate three-body recombination can be enhanced by at least several orders of magnitude especially on reducing pressure.

Of the nine elements in the first three columns of transition elements, all except V can be chemi-ionized by atomic oxygen at low temperatures and produce the M^+O ion. This exception by V is not unreasonable and simply relates to the gradual falloff of binding energy as one moves across the transition elements making it a marginal case.[20] Similarly, all the rare earth and actinide elements can produce the M^+O ion with the exceptions of Eu, Tm, and Yb. These exceptions likewise are not unusual for these elements. It reflects their known electronic configurational differences that affect these and quite often Sm as well in many of their other chemical interactions.[21]

Fortunately, although the available database is less complete for the energetics of reaction 3 to produce MO_2^+, it appears to be sufficient to show the same general trends. Exothermic cases are restricted to the same elements as for M^+O formation. However, this time the energetics are favorable to only a few of them. Nevertheless, it is feasible at low temperatures for at least five of the nine transition elements in the first three columns, namely, Zr, Nb, La, Hf, and Ta, but otherwise only for the initial rare earth and actinide elements, Ce, Pr, Th, U, and Np. More will be said of these specific MO_2^+ ion stabilities and lifetimes below.

V. Ion Relative Stabilities

Thermal Stabilities, MO and M^+O. As seen from the ionization potentials of the elements listed in Table 2, Cs has the lowest value at 376 kJ mol^{-1}. It ionizes readily in flames and for Cs additions of 10^{10} cm^{-3} at atmospheric pressure it will be 98% ionized at 2300 K after 1 ms. However, comparing this to sodium under the same conditions with its ionization potential of 496 kJ mol^{-1}, it is noted that only 0.8% of Na is ionized. Thermal ionization is critically controlled by the magnitude of the ionization potential and the temperature. For the MO species of interest here, the ionization potentials for MO and the dissociation enthalpies for M^+O are listed for comparison in Table 4. The smallest values for MO are those for CeO, PrO, and LaO at 473, 473, and 478 kJ mol^{-1}, respectively. These are magnitudes that compare closely to that seen in the example of elemental Na above. Other values increase to as high as 762 kJ mol^{-1} for TaO. Similarly, the enthalpy values for the dissociation of M^+O by its lower-energy channel to M^++O has very significant energy barriers to thermal dissociation for those elements that can exothermically chemi-ionize to form M^+O ions. Limited to solely considering these elements, the smallest value in Table 4 is 550 kJ mol^{-1} for Lu^+O. Consequently, at most temperatures where such chemi-ionizing processes might be invoked, contributions from thermal ionization and thermal dissociation will be negligible.

Thermal Stabilities, MO_2 and MO_2^+. Listed also in Table 4 are the enthalpy values for the thermal ionization of various MO_2 species. With the exceptions of UO_2 (591 kJ mol^{-1}) and

NpO_2 (611 kJ mol^{-1}), these are seen to be uniformly very large ruling out its role as an ionization channel. In comparison, the thermal stability of these MO_2^+ ions is quite different. With the exceptions of Eu, Tm, and Yb, which cannot chemi-ionize exothermically, their preferred thermal dissociation channel is to $M^+O + O$ with the result that some of them have low-energy barriers and in some systems the MO_2^+ will decay to M^+O thermally. Of the 10 cases where chemi-ionization by reaction 3 is exothermic, or close to thermoneutrality and these ions can be produced, enthalpy values for the thermal dissociation are the smallest for LaO_2^+(190), CeO_2^+(191), and PrO_2^+(212 kJ mol^{-1}). The others are thermally very stable with UO_2^+ very much so.

Potential Ion Exchange Channels for M^+O. The possibility has been outlined above whereby M^+O and MO_2^+ ions can be produced by chemi-ionization reactions in oxygen plasmas at low temperatures and may be immune to electron recombination by the reverse of their formation reactions. Nevertheless, other reactions such as reactive charge transfer may still occur. One such reaction to consider is

$$M^+O + O_2 = MO_2^+ + O \quad \Delta H(5) = \Delta H(3) - \Delta H(2) \qquad (5)$$

By comparison of the enthalpy values for reactions 2 and 3 in Table 3, the enthalpy of reaction 5 can immediately be noted. If the value for M^+O formation is more negative (more exothermic) than that for MO_2^+ formation, then reaction 5 will be endothermic and, of the two ions, M^+O generally will be favored. As a result, it is seen that only in the four cases of Nb, Ta, U, and Np will MO_2^+ formation be favored and any initially produced M^+O for these elements will convert to the dioxide ion. In fact, this has been reported already in ion-trap and ion-flow tube work.[22−24] Moreover, for three of these, the measured rate constants for reaction 5 reflect approximately unit gas kinetic collision efficiencies.[22−24]

Another possibility to consider is whether these molecular ions can reactively transfer their charge solely onto the element. Table 1 lists the energetics of reaction 6

$$M^+ + O_2 = M^+O + O \qquad (6)$$

Negative enthalpies (exothermic) imply a preference for the oxide ion. Consequently, in all the 18 cases mentioned above where the diatomic oxide ion is not converted to the dioxide it is seen from Table 1 that they will retain their M^+O nature and not convert to M^+.

As observed in the published literature, reaction 6 has been much studied. In cases where it is exothermic, emphasis has been on measuring kinetic rate constants. These have been obtained for reaction 6 for all those elements of prime interest here, namely, the nine transition elements in their first three columns of the periodic table and for all the rare earth elements that can chemi-ionize to M^+O.[23−32] These are uniformly very efficient reactions with rate constants at 298 K that lie in the close range of values of (2.4−8.5) × 10^{-10} cm^3 molecule^{-1} s^{-1} with only Lu^+ slower at 7×10^{-11}. These values reflect reactions that proceed at essentially every collision or a high fraction of collisions. Additionally they appear to be insensitive to temperature.[24−28] These studies also are noteworthy in that they additionally illustrate alternate methods for forming the M^+O ions directly from M^+.

In a complimentary manner, those reactions in Table 1 indicating that reaction 6 is endothermic have also been put to good use. Primarily examined by Armentrout et al., using guided ion beam techniques, they developed a method to obtain the then either unknown or very uncertain values for the bond strengths of M^+O ions. These were derived by determining the onset threshold energies needed for reaction 6 to occur. In this way they have measured D(M^+O) values for 22 such ions that include alkaline earths,[29,33] transition elements,[29,34−36] and Al.[37] Many of these values are summarized in a recent review. [38]

Although Koyanagi et al.[24] did report the formation of higher oxide ions such as MO_3^+ for Ti, Y, and Zr (but not for Sc or La) in such oxide ion systems, these were only seen at higher oxygen pressures. Moreover, they were formed by much slower three body interactions such as reaction 7

$$M^+O + O_2 + Z = MO_3^+ + Z \qquad (7)$$

Consequently, such complications in studies of these M^+O long-lived ions can easily be avoided.

Potential Ion Exchange Channels for MO_2^+. Being a polyatomic ion, the kinetic options are several for any MO_2^+ that can be produced exothermically by reaction 3. One preferred channel for six (Zr, La, Hf, Ce, Pr, Th) of the 10 such elements is to convert to M^+O by the reverse of reaction 5. Although it was indicated earlier that these dioxide ions could not dissociatively recombine with an electron via the reverse of reaction 3, being a polyatomic ion they do have a second alternate dissociative recombination channel back to MO, namely, reaction 8

$$MO_2^+ + e^- = MO + O \quad \Delta H(8) = \Delta H(1) - \Delta H(3) \qquad (8)$$

An examination of the values listed for reaction 1 and 3 in Tables 1 and 3 indicates that the energetics are more favorable for this and effective recombination will occur for nine of the ten cases, the single exception being UO_2^+. Consequently, six elements (Zr, La, Hf, Ce, Pr, Th) have two simultaneous options, conversion of the MO_2^+ ion to M^+O by reaction with O atom (reaction 5) and dissociative recombination with electrons to MO (reaction 8). If the temperature is slightly elevated, a contribution from thermal dissociation of LaO_2^+, CeO_2^+, and PrO_2^+ to the M^+O ion also can occur as mentioned already from Table 4. Three others (Nb, Ta, and Np) will rapidly decay solely by this alternate dissociative recombination channel. Only UO_2^+ of the dioxide ions will be extremely stable both chemically and thermally, decaying slowly by a three-body interaction. This long lifetime for UO_2^+ has been noted and observed previously.[22,39]

Chemi-Ionization-Facilitated Thermal Ionization. There is another interesting aspect of the values in Tables 1 and 3 in connection with M^+O ions that does not relate directly to the present discussion but might be borne in mind in considerations of other metal elements of the periodic table. Namely, if an M^+O ion is formed via an endothermic chemi-ionization reaction 2 by applying external energy, although it will be prone to rapid dissociative recombination with electrons, it additionally has the possibility of reactive branching with conversion either to MO_2^+ or M^+. By consideration first of the case of V, which is in the first three columns of the transition elements but is the one exception being endothermic toward chemi-ionization. If the deficit energy is supplied, it can chemi-ionize via reaction 2 forming V^+O. The tables then indicate that this can dissociatively recombine to the element but can convert neither to V^+ via reaction 6 nor to VO_2^+ by reaction 5. However, for many of the other elements in the periodic table a different behavior is possible. This is the case also for the three rare earths, Eu, Tm, and Yb, that were the exceptional rare earths exhibiting

TABLE 5: Available Relative Rate Constant Values (cm^3 $molecule^{-1}$ s^{-1}) for Exothermic Chemi-Ionization Reactions 2 and 3 and the Competing Exothermic Oxidation Reaction 1

$M + O = M^+O + e^-$ (2)			$M + O_2 = MO + O$ (1)			
M	$k_{298K}(2)$	ref	$k(1)$	$k_{298K}(1)$	ref	k_2/k_1 (298 K, %)
Y	1.5×10^{-11}	39	$2.2 \times 10^{-10} \exp(-421/T)$	5.4×10^{-11}	43	28
La	3.5×10^{-10}	39	$4.0 \times 10^{-10} \exp(-373/T)$	1.1×10^{-10}	44	318
Ti	1.7×10^{-12}	41	$1.7 \times 10^{-10} \exp(-1395/T)$	1.6×10^{-12}	45	105
Zr	6.0×10^{-11}	41	$2.6 \times 10^{-10} \exp(-746/T)$	2.1×10^{-11}	46	286
Ce	6.7×10^{-12}	39	$3.0 \times 10^{-10} \exp(-409/T)$	7.6×10^{-11}	44	9
Pr	1.3×10^{-10}	39	$3.1 \times 10^{-10} \exp(-637/T)$	3.7×10^{-11}	44	351
Nd	1.7×10^{-10}	39	$3.6 \times 10^{-10} \exp(-746/T)$	2.9×10^{-11}	44	577
Sm	9.9×10^{-12}	39	$2.4 \times 10^{-10} \exp(-746/T)$	2.0×10^{-11}	44	50
Gd	4.5×10^{-11}	41	$2.7 \times 10^{-10} \exp(-625/T)$	3.3×10^{-11}	44	136
Dy	5.0×10^{-13}	39	$2.8 \times 10^{-10} \exp(-1094/T)$	7.1×10^{-12}	44	7
Er	4.7×10^{-14}	39	$3.0 \times 10^{-10} \exp(-1275/T)$	4.2×10^{-12}	44	1
Th	7.2×10^{-11}	41				
U	1.0×10^{-10}	39		8.5×10^{-11}	47	117
$M + O_2 = MO_2^+ + e^-$ (3)			$k(1)$	$k_{298K}(1)$		k_3/k_1, (298 K, %)
La	8.4×10^{-13}	39	$4.0 \times 10^{-10} \exp(-373/T)$	1.1×10^{-10}	44	0.8
Ce	1.5×10^{-14}	39	$3.0 \times 10^{-10} \exp(-409/T)$	7.6×10^{-11}	44	0.02
Pr	1.9×10^{-14}	39	$3.1 \times 10^{-10} \exp(-637/T)$	3.7×10^{-11}	44	0.05
Th	8.1×10^{-13}	41				
U	1.9×10^{-12}	42		8.5×10^{-11}	47	2.2

endothermic chemi-ionization. Namely, taking Cr, the neighbor of V, as an example, this can be chemi-ionized with O to Cr^+O if 300 kJ mol^{-1} of energy is provided. This will both dissociatively recombine with an electron to reproduce Cr and react via the reverse of reaction 6 to produce a long-lived Cr^+ ion. It cannot channel to CrO_2^+. The resulting Cr^+ ions undoubtedly may not be produced in high yield, but nevertheless, these atomic ions will have been formed at a lower temperature than that needed to otherwise overcome the 653 kJ mol^{-1} direct thermal ionization energy barrier of Cr. This is of somewhat academic interest but because many of the values for reaction 6 are positive in Table 1, and the enthalpies of reaction 3 are generally larger than for reaction 2, such potential conversion of M to M^+ via M^+O is a general mechanistic possibility. It appears not to have been invoked in metal/oxygen systems. However, in flames, it is conceivable that the observed levels of M^+ ions for Ca, Sr, and Ba arise predominantly from a similar type of chemi-ionization reaction. For example, Sr is chemi-ionized endothermically to a $SrOH^+$ intermediate that then recombines with electrons but also reacts with H atoms to form Sr^+. In this way, it facilitates the Sr/Sr^+ ionization much faster than the direct thermal ionization channel.[16,40]

VI. Reactions of Neutrals and Ionization Efficiencies

Chemi-ionization reactions generally are a subset within a number of other reactions. As indicated already by reaction 1 and its exothermic nature shown in Table 1, the basic oxidation of an atomic metal to MO and subsequently further in most cases to MO_2 is an alternate and generally more dominant channel than that of ionization. Moreover, such oxidation then decommissions the elemental metal from further interaction. Consequently, due to the energetic nature of those elements that can lead to long-lived M^+O ions, it can be expected that chemiluminescent competing channels will accompany the chemi-ionization reaction. By consideration of the case of a gaseous metal in an oxygen plasma, the efficiencies of ion production will depend partly on the relative kinetic rate constants. Table 5 lists the available kinetic data for the chemi-ionizing reactions 2 and 3. Generally, the efficiencies are much larger for reaction 2 and the values do not appear to be sensitive to temperature.[25,48,49] For comparison, the rate constants for reaction 1 also are listed. In terms of reaction cross section, the chemi-ionizing reaction with atomic oxygen is seen to be very efficient in many of the cases listed. That for Nd is almost 600 times larger than the neutral reaction with O_2. This will be offset in actual reactive flux by the fact that O_2 concentrations will generally be larger than atomic oxygen but nevertheless it is seen that these ionizing channels can be significant. With the exception of U, those involving O_2 by reaction 3 are less efficient and will be of minor significance.

Consequently, for Sc, Ti, Y, Zr, La, and Hf, the 11 rare earth elements indicated above, and possibly Th, chemi-ionization via reaction 2 can produce long-lived ions relatively efficiently.

VII. Relative Lifetimes of These Potentially Long-Lived MO^+ Ions

A more detailed examination of the enthalpies listed in Table 3 for the chemi-ionizing reaction 2 and their associated error bars helps to better characterize the relative stabilities of these potentially long-lived ions. Consequently, that for Sc^+O formation (-56 ± 14 kJ mol^{-1}) is sufficiently accurate and of a magnitude that this ion will not effectively recombine by dissociative recombination except at moderate temperatures. Such an energy barrier for the reverse direction of the reaction, at 600 K for example, slows kinetic rates by a factor of 5 orders of magnitude. More exothermic values than this eliminate the possibility of dissociative recombination altogether. As a result, it should be possible to produce Sc^+O in room temperature oxygen plasmas and its lifetime will be very significantly enhanced over that of normal molecular cations. By the same argument, this is even more so for Y^+O (-109 ± 15), La^+O (-319 ± 50), Zr^+O (-109 ± 10), Hf^+O (-69 ± 15), Ce^+O (-317 ± 12), Pr^+O (-274 ± 25), Nd^+O (-215 ± 15), Pm^+O (-123 ± 50), Gd^+O (-153 ± 15), Tb^+O (-178 ± 20), and Th^+O (-237 ± 10 kJ mol^{-1}). The remaining six elements that have exothermic reactions and have been included in the discussion up to this point are marginal. For example, these have corresponding enthalpy values of Ti^+O (-5 ± 7), Sm^+O (-27 ± 15), Dy^+O (-15 ± 20), Ho^+O (-5 ± 25), Er^+O (-1 ± 15), and Lu^+O (-27 ± 30 kJ mol^{-1}). These magnitudes imply formation reactions that are somewhat close to thermal neutrality and so have an ease of reversibility. The apparent exothermicity of Sm is supported also by the chemielectron spectrum for Sm^+O formation.[50] Moreover, as listed in Table 5, rate constants for this chemi-ionization channel with Ti, Sm, Dy, and Er have been reported and are not too different from those needs changing to that with Ce in the first two cases but are much reduced with Dy and Er. With the exception of Ti, these rare earth elements include Sm, mentioned previously as often being grouped with Eu, Tm, and Yb due to its electronic configuration, and the other four constitute the high atomic number members Dy, Ho, Er, and Lu of the rare earth elements.

As a result, it appears that only twelve elements of the periodic table can form M^+O ions that, as seen in Table 4, are both extremely thermally stable ($D(M^+{-}O) = 662{-}857$ kJ mol^{-1}) and exhibit a reluctance to charge neutralize except by slow three-body recombination kinetics.

VIII. Previous Studies that Have Examined These Diatomic Oxide Ions

There have been numerous studies already that have reported the presence of these ions. Monitoring has been either by mass spectrometry, by infrared absorption, by electron spin resonance (ESR), or by chemielectron or photoelectron spectroscopy. In a series of experiments, Goodings et al. have examined the ionic nature of several of these elements in flames using mass spectrometric sampling. Of those relevant to this study, similarity of behavior was noted for the elements Sc, Y, La, Ce, Pr, and Nd.[51−55] All displayed M^+O as the dominant flame ion with no evidence of MO_2^+ formation. This is as predicted herein and any such MO_2^+ that might be formed will immediately be converted to the diatomic ion or decay with electrons. Also, because the ionization potential of ScO is about 612 kJ mol^{-1}, thermal ionization is negligible and chemi-ionization has to be the dominant formation mechanism in these flames. Because they all behave similarly it is undoubtedly playing a major role in these cases. Most interesting is the fact that the ion profiles through the burned gases of the atmospheric pressure flame are long-lived and decay very slowly through the observed milliseconds time scale. Also, the production of ions is more rapid than seen for thermally ionizing alkali elements, but the decay rates are symbolic of slow three-body recombination that is on such a time scale.

In low-pressure crossed-beam studies, Dyke et al. have examined the chemi-ionization reactions of La, Ce, Pr, Nd, Sm, and Gd with O and $O_2(a^1\Delta_g, X^3\Sigma_g^-)$ monitoring the chemielectron and ion mass spectra.[50,56] Their observations of both oxide ions for La, Ce, and Pr, but only the M^+O ion with Nd, Sm, and Gd are as predicted here. Their observation of LaO_2^+ and the electron energy spectrum, coupled with data of others, has helped to resolve some of the uncertainties that remain concerning the ionization potential and bond energy of LaO_2. The enthalpy value for reaction 3 listed in Table 3 is based on estimates from such studies. The fact that the reaction has been observed by Dyke et al. and as seen in Table 5 has a reasonable cross section supports its exothermicity.

Andrews et al. in a series of studies have examined the products resulting from the reactions between laser-ablated metals with oxygen in argon matrixes that were subjected to mercury ultraviolet photolysis. The products were monitored by infrared absorption, and labeled oxygen was used to facilitate identification. In this way, vibrational frequencies and bond lengths have been assigned to numerous metal monoxide ions and several dioxide ions. In two papers, Willson and Andrews[57,58] examine the interactions between oxygen and the rare earths. They observed all the rare earth M^+O ions with the exception of Pm, which was not studied, and includes those also for Eu, Tm, and Yb. These latter interactions tend to illustrate some role of the metal or oxygen in their excited states in the chemi-ionization. From these elements, they only assigned dioxide ion vibrational bands to PrO_2^+, NdO_2^+, and HoO_2^+. Interestingly, it is surprising that they did not similarly assign CeO_2^+ and that these did not fully convert to their respective M^+O ions. Moreover, the formation and tentative assignment of bands to HoO_2^+ would appear to be unlikely considering the expected trends and thermodynamic values now apparent. In studies of those transition elements of interest here, that with Sc indicated no metal ions.[59] It was suggested that any Sc^+O ion formed reacted with NO_2 losing its charge and forming NO^+ instead. In the case of V, no metal ions were assigned.[60] With U, the UO_2^+ ion was the only metal ion assigned.[61] In a similar manner, Chen et al.[62] assigned vibrational frequencies to Ta^+O and TaO_2^+ in laser ablation/matrix isolation studies with Ta_2O_5 or Ta in O_2/Ar mixtures.

The pronounced thermal stabilities noted earlier of ions such as Y^+O, La^+O, Ce^+O, and Lu^+O, when coupled to their chemi-ionization nature, can have noteworthy implications for inductively coupled plasma (ICP) monitors. For such instruments, in the 5000 K temperatures of the Ar plasma that is rich in electrons, dynamic kinetic balances will exist for these chemi-ionization and dissociation reactions such that, even with Lu, it will be in constant flux, existing in Lu, Lu^+, LuO, LuO_2, and Lu^+O forms. As a result these elements have been discussed at length in the analytical literature due to their potential as interferents.[63−65] Techniques have been suggested for example to minimize the La^+O/La^+ ratio and resolve such complications.[66,67]

Additionally, these ions have been reported in the plumes of numerous laser-ablation studies. By use of mass spectrometric monitoring, Y^+O is reported using a $YBa_2Cu_3O_y$ target,[68] La^+O from $La_{1-x}Ca_xMnO_3$ thin films,[69] TiO^+ from a TiO_2 film,[70] and Ta^+O and TaO_2^+ from Ta_2O_5 targets.[71] Gibson[72] noted the interesting observation that laser ablation of Yb_2O_3 generated only polyatomic ions, whereas the corresponding ablation of Ln_2O_3 (Ln = Sm, Eu, Gd, Dy) produced only Ln^+ or Ln^+O ions. Photofragmentation of vanadium oxide cluster cations was shown to ultimately produce V^+O and VO_2^+ ions.[73] Also of significance, Fried et al.[74] observed in ablating Y_2O_3 in O_2 that with the application of electric fields two luminous plumes could be produced.

Consequently, there appears to be significant support for the enthalpy values of the chemi-ionization channels derived from this analysis. The thermochemical databases for these oxides and oxide ions still have significant error bars in some cases but fortunately these are not large enough to interfere with the interpretations that have been made. Additionally, the value of observing trends in large collections of data, particularly spanning the whole periodic table has become very evident in this work.

IX. Implications for Spectroscopic Characterization

Because of the normal short lifetime of molecular ions and the complication of spectrally resolving systems that contain both spectra of the neutral MO and the ion M^+O, very few metal ion spectra have been assigned. The introduction of the Velocity Modulation Technique 20 years ago by Saykally et al. has overcome to a large degree the discrimination problem. Nevertheless, as noted from a very extensive recent review by them of the technique,[75] even though many molecular ions have been analyzed, with the single exceptions of Ti^+Cl and Ti^+F they remain all nonmetallic. Of the ions of interest to this paper only a few optical spectroscopic studies are reported at all. ESR spectra of Zr^+O and Hf^+O have established their $^2\Sigma$ ground-state configurations.[76] Spectral analyses of near-infrared emission have been assigned to transitions for the $Zr^+O(A^2\Pi - X^2\Sigma^+)$ system.[77,78] Pulsed-field ionization of VO has probed the $V^+O(^3\Sigma^-, v = 0)$ state,[79] and two $^1\Sigma - ^1\Sigma$ and $^1\Delta - ^1\Delta$ near-infrared transitions were resolved by their Fourier transform infrared emission and assigned to V^+O.[80] REMPI/Photoelectron spectra have noted $Ti^+O(B^2\Sigma^+, A^2\Sigma^+, X^2\Delta)$ states.[81,82] Similarly, few theoretical studies have appeared, but some report on the nature of the electronic states of V^+O[83−85] and La^+O.[86] Kretzschmar et al.[87] have listed the ground-state configurations of Sc^+O, Ti^+O, V^+O, Y^+O, Zr^+O, and Nb^+O ions.

Recently, Dyke et al. have completed for the first time two theoretical studies constructing the potential-energy curves for SmO, Sm^+O,[88] and UO and U^+O electronic states[89] in relation to their atomic chemi-ionization reactions with atomic oxygen. This has begun the process of understanding the details of the autoionization mechanism involved in such chemi-ionization interactions. Identification of the specific states involved is helped and likewise facilitates the interpretation of the chemielectron band energy spectra that they have observed for such systems.

The fact that stable ions now can be formed that have much enhanced lifetimes, coupled to velocity modulation, should enable this class of metal oxide ions to be spectrally characterized in detail. Moreover, a single cell that is subjected to both the formation discharge and the modulating field is no longer necessary and the two stages of formation and monitoring can be better separated for experimental ease.

The spectral characterization of neutral MO molecules for the transition elements is quite extensive and has been tabulated up to the late 70s in the reference book of Huber and Herzberg.[90] Numerous additional studies since have been added. Consequently by invoking the useful concept of isoelectronic and isovalent comparisons, the spectral locations and assignments expected for spectroscopic transitions of a particular M^+O ion can be predicted to some degree. Two examples of such isoelectronic comparisons consider the states of ScO, TiN, CaF, and VC and explains their observed differences.[78,91] These in fact are isoelectronic also with Ti^+O. Balfour and Lindgren[78] more relevantly show a comparison between the (B, A) states of isoelectronic Zr^+O, YO, SrF, and ZrN and some of their isovalent analogues, and the way this method can aide in spectral analysis. More recently, the pairs ScO, TiN and YO, ZrN have been compared in a discussion of their $B^2\Sigma^+$ states.[92] In connection with the present paper, Figure 1 illustrates the numerous singlet and triplet states known for CaO,[93−96] SrO,[90,97,98] and BaO,[90,99,100] which are isoelectronic with Sc^+O, Y^+O, and La^+O, respectively. It similarly shows the energy locations of known states for ScO,[90,101] YO,[90,92,102,103] and LaO,[104,105] which are isoelectronic with Ti^+O, Zr^+O, and Hf^+O. Similar type electronic transitions can be expected for these ions. Obtaining such experimental values would help in the validation and further development of spectroscopic theory for such ionic systems.

Moving into the spectroscopic nature of rare earth oxides introduces significantly more complexity due to the higher density and more varied spin multiplicities of possible states. Nevertheless, as reviewed by Balasubramanian[106] and Dulick et al.,[107] the success of ligand field theory has helped to predict and assign the numerous electronic states of MO. As a result potential comparisons between isoelectronic LaO and Ce^+O and between CeO with its single 4f electron and Pr^+O would be rewarding. The complexities of the other rare earths are very significant, but this has not prevented numerous experimental and theoretical studies of their neutral MO states. Moreover, it is within the capability of theory to endeavor now to make the same predictions but for these M^+O molecules.

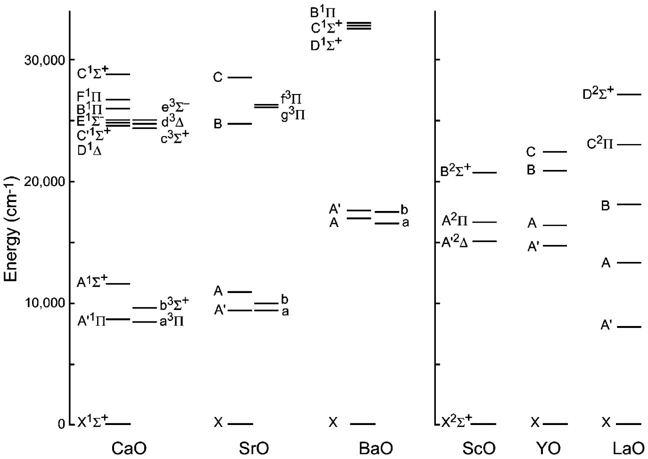

Figure 1. The energies of the various low-lying electronic states characterized for these neutral MO oxides.

X. Conclusions

As a result of an extensive analysis of thermochemical values, a unique series of diatomic metal oxide ions has become apparent in the periodic table that are long-lived. For molecular ions this is somewhat unique and a fact not widely realized. It now opens the possibility of characterizing their electronic states, determining their thermochemical properties, and establishing their electronic configurations. Previously such ions have been monitored generally by mass spectrometric techniques or only their ground states examined spectrally. The elements involved that can be successfully chemi-ionized by atomic oxygen to these M^+O ions are found in the first two columns of the transition elements, the rare earth elements, and Th. Of these 18 elements, 12 (Sc, Y, La, Zr, Hf, Ce, Pr, Nd, Pm, Gd, Tb, Th) are predicted to have long-lived monoxide ions, immune to dissociative recombination with electrons and as with atomic ions must utilize a slow three-body recombination mechanism with electrons for charge neutralization. The other six (Ti, Sm, Dy, Ho, Er, Lu) can chemi-ionize at low temperatures by marginally exothermic reactions such that the reverse dissociative recombination may still contribute to their decay and consequently shorten their lifetimes. Chemi-ionization reactions that produce MO_2^+ ions also are included in the analysis, but of these UO_2^+ is singularly unique. It is both long-lived, being similarly immune to dissociative recombination, and is thermally very stable.

Acknowledgment. The author is grateful for the support provided over a number of years from the Aerophysics Department of the General Motors Corporation, Santa Barbara Operations, and from the Arnold Engineering Development Center, Air Force Materiel Command, Arnold Air Force Base, Tennessee, both of which enabled this program to be developed. The work has been completed using the Materials Research Laboratory Central Facilities that is supported by the National Science Foundation under Award No. DMR00-80034.

References and Notes

(1) Trautz, M. *Z. Elektrochem.* **1908**, *14*, 453.
(2) Behrens, H. *Naturwissenschaften* **1951**, *38*, 187.

(3) Blades, A. T. *J. Chromat. Sci.* **1973**, *11*, 251.

(4) Scanion, J. T.; Willis, D. E. *J. Chromat. Sci.* **1985**, *23*, 333.

(5) Huang, Y.; Ou, Q.; Yu, W. *Anal. Chem.* **1990**, *62*, 2063.

(6) Fontijn, A.; Golomb, D.; Hodgeson, J. A. In *Chemiluminescence and Bioluminescence*; Cormier, M. J., Hercules, D. M., Lee, J., Eds.; Plenum Press: New York, 1973; pp 393−426.

(7) *Gas-Phase Chemiluminescence and Chemiionization*; Fontijn, A., Ed.; Elsevier Science: Amsterdam, 1985.

(8) Eletskii, A. V.; Smirnov, B. M. *Sov. Phys. Usp.* **1982**, *25*, 13.

(9) McGowan, J. W.; Mitchell, J. B. A. In *Electron−Molecule Interactions and Their Applications*; Christophorou, L. G., Ed.; Academic Press: Orlando, 1984; Volume 2, Chapter 2, pp 65−88.

(10) Adams, N. G. In *Advances in Gas-Phase Ion Chemistry*; Adams, N. G., Babcock, L. M., Eds.; Jai Press: Greenwich CT, 1992; Volume 1, pp 271−310.

(11) Schofield, K. *Electron Generation Resulting from the Ablation of Various Metals into Wakes of Subscale Vehicles: An Assessment*; Aerophysics Department, General Motors Corporation, Santa Barbara Operations, Report SD-TR-79-21, 1978; pp 1−98.

(12) Schofield, K. *Electron Generation and Decay Processes in Ballistic Wakes and Thermal Plasmas*; Arnold Engineering Development Center, Air Force Materiel Command, Arnold Air Force Base, Tennessee, Report AEDC-TR-93-8, 1994; pp 1−60.

(13) Spence, M. A.; Tomlinson, W. R.; Levy, M. R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3610.

(14) Higashiyama, T.; Ishida, M.; Matsumoto, Y.; Honma, K. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2481.

(15) Dickson, C. R.; Zare, R. N. *Chem. Phys.* **1975**, *7*, 361.

(16) Schofield, K.; Sugden, T. M. *Proc. Combust. Inst.* **1965**, *10*, 589.

(17) Gousset, G.; Sayer, B.; Berlande, J. *Phys. Rev. A* **1977**, *16*, 1070.

(18) Alkemade, C. Th. J.; Hollander, Tj.; Snelleman, W.; Zeegers, P. J. Th. *Metal Vapors in Flames*; Pergamon Press: Oxford, 1982.

(19) Davidson, D. F.; Hobson, R. M. *J. Phys. B: At. Mol. Phys.* **1987**, *20*, 5753.

(20) Armentrout, P. B.; Kickel, B. L. In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer Academic: Dordrecht, 1996; Chapter 1, pp 1−45.

(21) Gibson, J. K. *J. Phys. Chem. A* **2003**, *107*, 7891.

(22) Lo, H. H.; Fite, W. L. In *Electronic and Atomic Collisions*; Takayanagi, K., Oda, N., Eds.; North-Holland: Amsterdam, 1979; pp 897−898.

(23) Matsuo, Y.; Maeda, H.; Takami, M. *Chem. Phys. Lett.* **1993**, *201*, 341.

(24) Koyanagi, G. K.; Caraiman, D.; Blagojevic, V.; Bohme, D. K. *J. Phys. Chem. A* **2002**, *106*, 4581.

(25) Johnsen, R.; Biondi, M. A. *J. Chem. Phys.* **1972**, *57*, 1975.

(26) Johnsen, R.; Castell, F. R.; Biondi, M. A. *J. Chem. Phys.* **1974**, *61*, 5404.

(27) Murad, E. *Int. J. Mass Spectrom. Ion. Process.* **1984**, *58*, 159.

(28) Dheandhanoo, S.; Chatterjee, B. K.; Johnsen, R. *J. Chem. Phys.* **1985**, *83*, 3327.

(29) Fisher, E. R.; Elkind, J. L.; Clemmer, D. E.; Georgiadis, R.; Loh, S. K.; Aristov, N.; Sunderlin, L. S.; Armentrout, P. B. *J. Chem. Phys.* **1990**, *93*, 2676.

(30) Koyanagi, G. K.; Bohme, D. K.; Kretzschmar, H.; Schroder, D.; Schwarz, H. *J. Phys. Chem. A* **2001**, *105*, 4259.

(31) Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2001**, *105*, 8964.

(32) Santos, M.; Marcalo, J.; Pires de Matos, A.; Haire, R. G. *J. Phys. Chem. A* **2002**, *106*, 7190.

(33) Dalleska, N. F.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Process.* **1994**, *134*, 203.

(34) Chen, Y.-M.; Armentrout, P. B. *J. Chem. Phys.* **1995**, *103*, 618.

(35) Sievers, M. R.; Chen, Y.-M.; Armentrout, P. B. *J. Chem. Phys.* **1996**, *105*, 6322.

(36) Zhang, X.-G.; Armentrout, P. B. *J. Phys. Chem. A* **2003**, *107*, 8904.

(37) Weber, M. E.; Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.* **1986**, *84*, 1521.

(38) Armentrout, P. B. *Int. J. Mass Spectrom.* **2003**, *227*, 289.

(39) Fite, W. L.; Patterson, T. A.; Siegel, M. W. *Cross Sections for Thermal Reactions Between Uranium Atoms and Atmospheric Species*; Air Force Geophysics Laboratory, Hanscom Air Force Base MA, Report No. AFGL-TR-77-0030, 1976; pp 1−88, NTIS Access No. AD/A 038806.

(40) Hayhurst, A. N.; Kittelson, D. B. *Proc. R. Soc. London A.* **1974**, *338*, 155.

(41) Lo, H. H.; Fite, W. L. *Chem. Phys. Lett.* **1974**, *29*, 39.

(42) Halle, J. C.; Lo, H. H.; Fite, W. L. *J. Chem. Phys.* **1980**, *73*, 5681.

(43) Campbell, M. L. *Chem. Phys. Lett.* **1998**, *294*, 339.

(44) Campbell, M. L. *J. Phys. Chem. A* **1999**, *103*, 7274.

(45) Campbell, M. L.; McClean, R. E. *J. Phys. Chem.* **1993**, *97*, 7942.

(46) Campbell, M. L. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1687.

(47) Lang, N. C.; Stern, R. C.; Finley, M. G. *Chem. Phys. Lett.* **1980**, *69*, 301.

(48) Fite, W. L.; Lo, H. H.; Irving, P. *J. Chem. Phys.* **1974**, *60*, 1236.

(49) Young, C. E.; Dehmer, P. M.; Cohen, R. B.; Pobo, L. G.; Wexler, S. *J. Chem. Phys.* **1976**, *64*, 306.

(50) Cockett, M. C. R.; Nyulaszi, L.; Veszpremi, T.; Wright, T. G.; Dyke, J. M. *J. Electron Spectrosc. Relat. Phenom.* **1991**, *57*, 373.

(51) Goodings, J. M.; Hassanali, C. S.; Patterson, P. M.; Chow, C. *Int. J. Mass Spectrom. Ion. Process.* **1994**, *132*, 83.

(52) Patterson, P. M.; Goodings, J. M. *Int. J. Mass Spectrom. Ion. Process.* **1995**, *148*, 55.

(53) Patterson, P. M.; Goodings, J. M. *Int. J. Mass Spectrom. Ion. Process.* **1996**, *152*, 43.

(54) Chen, Q.-F.; Goodings, J. M. *Int. J. Mass Spectrom. Ion. Process.* **1999**, *188*, 213.

(55) Guo, J.; Goodings, J. M. *Int. J. Mass Spectrom.* **2002**, *214*, 339, 349.

(56) Cockett, M. C. R.; Dyke, J. M.; Ellis, A. M.; Feher, M.; Wright, T. G. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *51*, 529.

(57) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 3171.

(58) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 6972.

(59) Chertihin, G. V.; Andrews, L.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Phys. Chem. A* **1997**, *101*, 9085.

(60) Chertihin, G. V.; Bare, W. D.; Andrews, L. *J. Phys. Chem. A* **1997**, *101*, 5090.

(61) Zhou, M.; Andrews, L.; Ismail, N.; Marsden, C. *J. Phys. Chem. A* **2000**, *104*, 5495.

(62) Chen, M.; Wang, X.; Zhang, L.; Yu, M.; Qin, Q. *Chem. Phys.* **1999**, *242*, 81.

(63) Tanner, S. D. *J. Anal. At. Spectrom.* **1993**, *8*, 891.

(64) Poussel, E.; Mermet, J.-M.; Deruaz, D. *J. Anal. At. Spectrom.* **1994**, *9*, 61.

(65) Nanose, N. S.; Matsuda, N.; Fudagawa, N.; Kubota, M. *Spectrochim. Acta B* **1994**, *49*, 955.

(66) Mei, Y.; Harrison, W. W. *Anal. Chem.* **1993**, *65*, 3337.

(67) Clemons, P. S.; Minnich, M. G.; Houk, R. S. *Anal. Chem.* **1995**, *67*, 1929.

(68) Zheng, R.; Campbell, M.; Ledingham, K. W. D.; Jia, W.; Scott, C. T. J.; Singhal, R. P. *Spectrochim. Acta B* **1997**, *52*, 339.

(69) Dang, H. J.; Han, Z. H.; Dai, Z. G.; Qin, Q. Z. *Int. J. Mass Spectrom.* **1998**, *178*, 205.

(70) Michiels, E.; Mauney, T.; Adams, F.; Gijbels. *Int. J. Mass Spectrom. Ion Process.* **1984**, *61*, 231.

(71) Wang, X.; Gu, Z.; Qin, Q. *Int. J. Mass Spectrom.* **1999**, *188*, 205.

(72) Gibson, J. K. *J. Phys. Chem.* **1994**, *98*, 6063.

(73) Kooi, S. E.; Castleman, A. W., Jr. *J. Phys. Chem. A* **1999**, *103*, 5671.

(74) Fried, D.; Kushida, T.; Reck, G. P.; Rothe, E. W. *Appl. Spectrosc.* **1994**, *48*, 248.

(75) Stephenson, S. K.; Saykally, R. J. *Chem. Rev.* **2005**, *105*, 3220.

(76) Van Zee, R. J.; Li, S.; Weltner, W., Jr. *Chem. Phys. Lett.* **1994**, *217*, 381.

(77) Phillips, J. G.; Davis, S. P. *Astrophys. J.* **1979**, *234*, 393.

(78) Balfour, W. J.; Lindgren, B. *Phys. Script.* **1980**, *22*, 36.

(79) Harrington, J.; Weisshaar, J. C. *J. Chem. Phys.* **1992**, *97*, 2809.

(80) Merer, A. J.; Cheung, A. S.-C.; Taylor, A. W. *J. Mol. Spectrosc.* **1984**, *108*, 343.

(81) Dyke, J. M.; Gravenor, B. W. J.; Josland, G. D.; Lewis, R. A.; Morris, A. *Mol. Phys.* **1984**, *53*, 465.

(82) Sappey, A. D.; Eiden, G.; Harrington, J. E.; Weisshaar, J. C. *J. Chem. Phys.* **1989**, *90*, 1415.

(83) Broclawik, E. *Int. J. Quantum. Chem.* **1995**, *56*, 779.

(84) Calatayud, M.; Silvi, B.; Andres, J.; Beltran, A. *Chem. Phys. Lett.* **2001**, *333*, 493.

(85) Calatayud, M.; Andres, J.; Beltran, A.; Silvi, B. *Theor. Chem. Acc.* **2001**, *105*, 299.

(86) Marquez, A.; Capitan, M. J.; Odriozola, J. A.; Sanz, J. F. *Int. J. Quantum. Chem.* **1994**, *52*, 1329.

(87) Kretzschmar, I.; Schroder, D.; Schwarz, H.; Armentrout, P. B. In *Advances in Metal and Semiconductor Clusters*; Elsevier Science: Amsterdam, 2001; Volume 5, pp 347−395.

(88) Paulovic, J.; Gagliardi, L.; Dyke, J. M.; Hirao, K. *J. Chem. Phys.* **2004**, *120*, 9998.

(89) Paulovic, J.; Gagliardi, L.; Dyke, J. M.; Hirao, K. *J. Chem. Phys.* **2005**, *122*, 144317.

(90) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

(91) Mattar, S. M. *J. Phys. Chem.* **1993**, *97*, 3171.

(92) Leung, J. W.-H.; Ma, T.; Cheung, A. S. C. *J. Mol. Spectrosc.* **2005**, *229*, 108.

(93) Norman, J. B.; Cross, K. J.; Schweda, H. S.; Polak, M.; Field, R. W. *Mol. Phys.* **1989**, *66*, 235.

(94) Baldwin, D. P.; Norman, J. B.; Soltz, R. A.; Sur, A.; Field, R. W. *J. Mol. Spectrosc.* **1990**, *139*, 39.

(95) Baldwin, D. P.; Field, R. W. *J. Mol. Spectrosc.* **1990**, *139*, 68.

(96) Baldwin, D. P.; Field, R. W. *J. Mol. Spectrosc.* **1990**, *139*, 77.

(97) Herrmann, R. F. W.; Sumnicht, G. K.; Stein, M.; Ernst, W. E. *J. Mol. Spectrosc.* **1992**, *156*, 487.

(98) Skelton, R. H.; Li, H.; Boone, C. D.; Le Roy, R. J.; Bernath, P. F.; Focsa, C.; Pinchemel. B. *J. Mol. Spectrosc.* **2003**, *219*, 1.

(99) Gottscho, R. A.; Weiss, P. S.; Field, R. W.; Pruett, J. G. *J. Mol. Spectrosc.* **1980**, *82*, 283.

(100) Gottscho, R. A.; Koffend, J. B.; Field, R. W. *J. Mol. Spectrosc.* **1980**, *82*, 310.

(101) Chalek, C. L.; Gole, J. L. *J. Chem. Phys.* **1976**, *65*, 2845.

(102) Simard, B.; James, A. M.; Hackett, P. A.; Balfour, W. J. *J. Mol. Spectrosc.* **1992**, *154*, 455.

(103) Bernard, A.; Gravina, R. *Astrophys. J. Suppl. Ser.* **1980**, *44*, 223.

(104) Bernard, A.; Sibai, A. M. *Z. Naturforsch.* **1980**, *35*, 1313.

(105) Carette, P. *J. Mol. Spectrosc.* **1990**, *140*, 269.

(106) Balasubramanian, K. *Relativistic Effects in Chemistry. Part B. Applications*; Wiley: New York, 1997.

(107) Dulick, M.; Murad, E.; Barrow, R. F. *J. Chem. Phys.* **1986**, *85*, 385.