

Chemistry of Barium Released at High Altitudes

by N. W. Rosenberg* and G. T. Best

*Air Force Cambridge Research Laboratories, L. G. Hanscom Field, Bedford, Massachusetts 01730
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Release of barium vapor at high altitude provides a useful geophysical tool by forming a visible tracer for motions of ions and neutrals in the ionosphere. The excitation, ionization, and oxidation of atomic barium released in sunlight between 100 and 200 km altitude is examined in this paper. Observed spectral measurements of resonance Ba and Sr atoms, excited Ba atoms, Ba ions, and BaO molecules provide the basis for estimating relative importance of the several processes. Excitation of ground-state barium to excited metastable levels with a time constant of 1 sec is followed by photoionization with a time constant of 30 sec. Oxidation of the metastables has an altitude-dependent time constant, ranging from a fraction of a second at 100 km to 40 sec at 200 km. Thus oxidation dominates over ionization at low altitudes and limits observations of ion clouds to altitudes above about 150 km.

Introduction

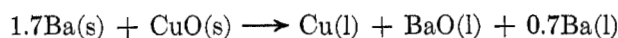
Chemical releases have been made into the earth's upper atmosphere for geophysical measurements for about 15 years. Released metal atom vapor reflects sunlight at its resonance radiation wavelengths, and can be photographed at twilight against the dark sky background. Injections of 1 kg of vapor can create a trail 1 km in diameter and 100 km long, the distortion and motion of which permit atmospheric winds to be derived from observations over a period of 100–1000 sec.

The release of barium vapor is a method of generating a high-density plasma in a sunlit upper atmosphere. Both neutral and ionized components resulting from the release may be separately tracked at twilight by ground-based optics in the light of their visible spectral emissions. The use of these releases to determine electric and magnetic fields and the dynamics of the atmosphere at altitudes from 160 km to several earth radii has been described in the literature.¹ The chemistry of the released barium vapor at high altitudes (where interaction with sunlight is the only factor in the kinetics) has also been discussed elsewhere,² but at altitudes below 200 km oxidation processes are also important. This paper will present recent data and interpretation concerning the competition between ionization and oxidation found in some 40 releases made in the last 5 years at heights from 95 to 200 km. The discussion is based on the time history of observed spectral emissions of four components: barium neutral, barium ion, barium oxide, and strontium neutral. The structure and composition of the upper atmosphere into which the barium vapor is released is defined by Table I.^{3,4} These values are subject to variations due to diurnal, seasonal, and solar effects, but serve to indicate that electron densities of more than 10^6 cm^{-3} would constitute a detectable perturbation of the iono-

sphere, while a corresponding initial barium density would be a minor constituent. In fact electron densities as high as 10^7 to 10^8 cm^{-3} have been achieved by the barium release technique.

Experimental Section

A few kilograms of a mixture of copper oxide and barium metal (1:1.7 mole ratio) is carried in a vaporizer aboard a rocket to the desired release point. Ignition at altitude results in substantially complete reaction within 30 msec to a 2500–3000°K liquid phase mixture of Cu, BaO, and Ba (and a small quantity of Ba vapor and outgassing products) at about 100 atm pressure. A



vented diaphragm is ruptured at 100 msec, and the entire canister contents are ejected (about 90% in 200 msec after vent.)

The vented material consists principally of barium vapor and liquid droplets of a mixture of barium, barium oxide, and copper (ground tests show that very little remains in the vaporizer). Barium vaporizes from the liquid droplets as the cloud of vapor and liquid moves along the rocket trajectory and expands radially, but cooling by radiation and evaporation reduces the vaporization to a negligible rate within 100 msec after release. The total barium vapor yield in our releases, which ranged from 2 to 6 kg of initial chemical mix, was between 7 and 10% of the original excess barium over a wide range of release altitudes and pay-

(1) G. Haerendel and R. Lust, *Sci. Amer.*, **219**, 80 (1968).

(2) G. T. Best and N. W. Rosenberg, "Spectroscopic Studies of Barium Release," paper presented at IAGA Symposium, Madrid, Sept 1969.

(3) U. S. Standard Atmosphere Supplements, U. S. Government Printing Office, Washington, D. C., 1966.

(4) COSPAR International Reference Atmosphere, North Holland, Amsterdam, 1965.

Table I: Structure of Upper Atmosphere^a

Altitude, km	Temperature, °K	$N(\text{Na})$, cm^{-3}	$N(\text{O}_2)$, cm^{-3}	$N(\text{O})$, cm^{-3}	$N(e)$, cm^{-3}	Collision frequency, sec^{-1}	Mean free path, cm
100	208	8.2 (12)	2.0 (12)	5.0 (11)	1 (5)	2.4 (3)	1.7 (1)
120	355	4.0 (11)	7.5 (10)	7.6 (10)	1.5 (5)	1.6 (2)	3.3 (2)
160	721	1.9 (10)	2.6 (9)	9.8 (9)	3 (5)	1.4 (1)	7 (3)
200	934	3.3 (9)	3.6 (8)	3.2 (9)	5 (5)	4.7 (0)	2.1 (4)

^a The number in parentheses is the exponent of 10, *i.e.*, 8.2 (12) = 8.2×10^{12} .

load sizes. There is an apparent increase in the yield of releases larger than 12 kg of chemical mix. In the experiments reported here, vaporized barium totaled about 1 mol, which would occupy about 0.1 km³ at ambient number density at 200 km.

A small quantity of vaporized barium oxide and barium ion is also observed in ground-state resonance lines in streak spectra for the first 200 msec. The barium metastable levels may also be thermally populated to a small extent, but are not seen because of the lower oscillator strengths of their "resonance lines".⁵

These transient features disappear as the spherical shell expands and the number density along the line of sight drops below the threshold for detection. After the vapor cloud has come to rest, a ring of particulate matter continues to expand with a radial velocity of 1 km sec⁻¹ perpendicular to the rocket trajectory and moves along the rocket trajectory with the original velocity of the rocket. This ring is identified as particulates because it scatters all wavelengths of the solar spectrum, even to the point of showing the solar Fraunhofer lines. A montage of photographs of a release is shown in Figure 1 and shows early time growth of vapor and particulates as well as late-time configurations of the ionized and neutral clouds.

Reaction Processes Following Release

The processes following the generation of a cloud of neutral barium vapor at high altitude in sunlight may be described qualitatively as excitation to metastable levels followed by the competing processes of ionization and oxidation. We shall now discuss each of these separately.

(a) *Excitation.* A partial term diagram of neutral barium is shown in Figure 2 and indicates the spectral features observed in emission from sunlit barium releases. Intensity data from spectra taken during the first 3 sec using $1/30$ sec resolution TV scanning are shown in Figure 3. Note that the ground-state resonance features of strontium and barium show a peak intensity at 0.1–0.3 sec, then falling rapidly to a more nearly constant level. This is believed to be due to the greater doppler width of the resonance lines before the cloud reaches thermal equilibrium with the ambient. The singlet and triplet metastable features are also seen to peak at about 1 sec after release. Optical

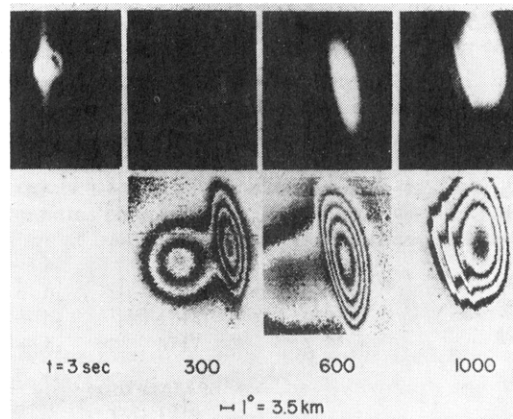
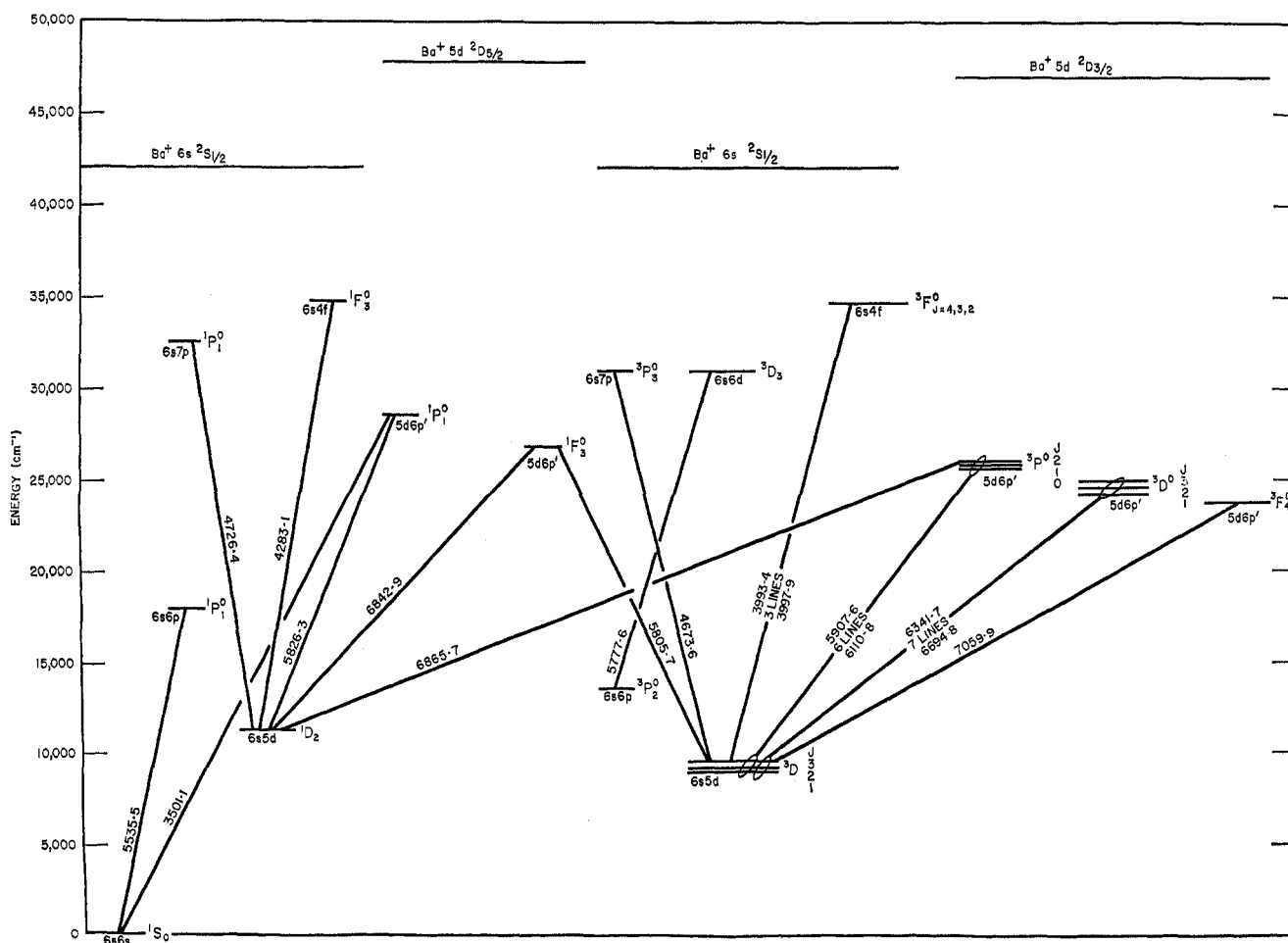


Figure 1. Montage of Ba release photographs. The lower row presents density contours of the unfiltered photographs above, and shows more clearly the weak neutral cloud. The 3-sec frame shows a neutral Ba sphere surrounded by a particulate ring. (The vertical line is caused by smearing of the bright central image in shutterless camera operation.) The 300-sec frame shows the separation of the ion cloud which has diffused preferentially along the earth's magnetic field lines from the spherical neutral cloud which is moving with the ambient wind. By this time, there is no significant Ba atom content remaining in the neutral cloud, which is scattering light only in Sr resonance and BaO band emissions. The 600-sec frame shows further separation, and development of a "bridge" connecting the ion cloud and the very weak neutral cloud. Spectroscopy shows that this bridge consists of ions, and is discussed in the text. The 1000-sec frame shows development of striations in the ion cloud by drift-caused instabilities.

pumping of the metastable ¹D level has been calculated to have a time constant of $\tau = 1.24$ sec, and it may be shown that solar irradiation will rapidly populate the 6s5d ³D metastable levels *via* the 5d6p' ¹F₃^o level ($\tau = 0.42$ sec) and *via* the 5d6p' ³P₂^o level ($\tau = 1.08$ sec). The 6s5d ³D₃ level is first populated but the multiplets between the ³D^o, ³P^o terms and the ³D term ensure rapid pumping of all ³D levels. The decay of 6s6p ³P₁^o (which is produced by the absorption of solar photons at 7911 Å) will also produce some metastable ³D barium atoms, but the time constants involved are 10–20 sec. The intensities of all the metastable lines decay as the barium ion lines grow in with the same time constant, which increases with altitude, asymptotically approach-

(5) B. M. Miles and W. L. Wiese, *Nat. Bur. Stand. (U. S.) Tech. Note*, No. 474 (1969).



Ba I TERM DIAGRAM

Figure 2. Term diagram of BaI showing emission features observed in sunlit high altitude releases.

ing 30 sec at altitudes above 260 km. This behavior will be explained in terms of removal of the neutral metastable barium by the competing processes of ionization and oxidation.

Strontium is present in the barium as a 1% contaminant, but displays only its resonance line at 4607 Å in these experiments. Because the 5s5p 3P term for strontium is lower than the 5s4d 3D term, the latter is not metastable in strontium, whereas the corresponding 6s5d 3D term for barium is lower than the 6s6p 3P term, and is metastable. If strontium were to ionize to any significant extent the SrII resonance lines at 4078 and 5215 Å would be seen. Likewise if significant SrO were produced the blue bands of the $B^1\pi-X^1\Sigma$ system would be seen.

(b) *Ionization.* As has been documented by Foppl, *et al.*,⁶ the reason for the choice of barium for the production of an ionized plasma was that the resonance lines of both neutral and ionized barium lay in the visible region of the spectrum. The expected time constant for solar photoionization from the ground state was estimated by Foppl, *et al.*, as 2000 sec⁻¹, due to both continuum photoionization and the exci-

tation of autoionizing levels. Using the recent cross section measurements of Hudson, Carter, and Young⁷ this estimate could be doubled, giving a photoionization time constant of about 1000 sec. The observed time constant for photoionization is in fact much closer to 30 sec, and is explained by a two-step process *via* one or more of the $1,3D$ metastable levels of barium. Consequently the wavelength required for photoionization is not 2380 Å, but in the region 3000–3260 Å, which provides a photon irradiance some 20–40 times greater in the solar flux, as shown in Table II.

The presence of strongly autoionizing levels in barium was first pointed out by Garton and Codling,⁸ who showed that the large photoionization cross section near the $6^2S_{1/2}$ limit was due to the presence of the 5d8p $^1P_1^\circ$ level close to the series limit, and which combined strongly with the $6s^2\ ^1S_0$ ground state. Autoionizing levels 5d9p and 5d10p $^3P_1^\circ$ were also noted in absorp-

(6) H. Foppl, G. Haerandel, J. Loidl, R. Lust, F. Melzner, B. Meyer, H. Neuss, and E. Reiger, *Planet. Space Sci.*, **13**, 95 (1965).

(7) R. D. Hudson, V. L. Carter, and P. A. Young, *Phys. Rev. A*, **2**, 643 (1970).

(8) W. R. S. Garton and K. Codling, *Proc. Phys. Soc.*, **75**, 87 (1960).

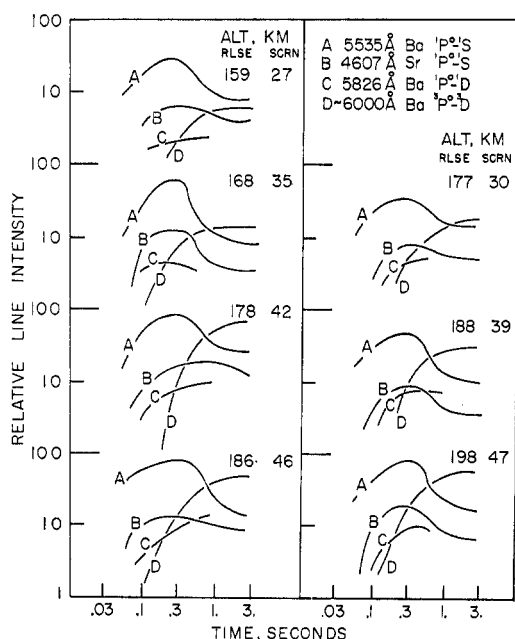


Figure 3. Relative intensities of spectral features of a barium release in the first 3 sec obtained by a slitless TV spectrograph.

Table II: Integrated Solar Photon Irradiance $\int_0^\lambda \theta_\lambda d\lambda$ above the Earth's Atmosphere

Wavelength λ , Å	Integrated photon irradiance, photons $\text{cm}^{-2} \text{sec}^{-1}$
2200	5.0 (13)
2400	1.6 (14)
2600	3.5 (14)
2800	9.0 (14)
3000	2.3 (15)
3200	4.6 (15)
3400	8.1 (15)

tion from the ground state. A subsequent attempt to find transitions from the metastable $5d6s\ ^1,^3D$ levels to these autoionizing levels failed to detect any significant lines.⁹ It thus appears probable that the photoionization is due to continuum absorption by one or more of the $1,^3D$ metastable levels. An attempt to isolate the particular level responsible, using the selective ultraviolet absorption of atmospheric ozone, has been reported elsewhere.² In the experiments described the earth's ozone layer was used to screen selectively, as a function of release altitude and solar depression angle, various wavelengths of solar radiation. The experiments were designed to find how late in evening twilight a barium release would still generate ion clouds. The rate of production of ions under various release conditions was measured and compared with rates computed according to various assumptions regarding the photoionization process. The conclusion was that both the $1D$ and $3D$ levels made significant

contributions to the rate of photoionization. However, the natural lifetime of the $1D$ level is reported to be 0.5 sec,^{10a} so it is concluded that the major source of ions is the $3D$ metastable term.

(c) *Oxidation.* At release the Ba inventory is almost entirely ground state. By times of the order of 1 sec (Figure 3) the neutral cloud is found to emit at wavelengths corresponding to ground state and metastable Ba, but only ground-state Sr (present as an impurity). By times of the order of 100 sec, the neutral cloud has lost all of its atomic Ba emissions and is radiating only in BaO bands and the ground-state atomic Sr line. Barium atoms disappear as the result of two competing processes, one of which is seen to be photoionization. Correcting for the fixed photoionization rate we may determine the altitude dependence of the other process from the observed rate of neutral disappearance. We find that over a large altitude (*i.e.*, density) range this rate constant is directly proportional to the number density of O_2 , with a two-body rate coefficient of $0.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. This rate coefficient is sufficiently large to indicate that the activation energy is small.

The bond strength of BaO is most recently reported by Gaydon^{10b} as 5.7 eV, which makes the $Ba + O_2$ reaction exothermic by 0.6 eV. However, metastable barium oxidation will be exothermic by an additional 1.2 eV and, because of the electronic excitation, may have a significantly lower activation energy. Reaction between barium and atomic oxygen is believed to be insignificant because it would require three-body collisions, which are too infrequent above 120 km.

We believe that oxidation by O_2 involves metastable rather than ground-state barium since the Sr present, which has no metastable levels, persists with no evidence for oxide formation. The slitted spectrograph which was used to give time-resolved atomic line spectra could not detect the barium oxide band spectrum with sufficient time resolution to determine directly the rate of barium oxide formation as a function of altitude. However, it has been determined that low-altitude releases form dense oxide clouds and the quantity of oxide produced decreases with increasing altitude. Additional evidence for the role of O_2 in oxidizing atomic barium comes from the laboratory measurements of Sakurai, Johnson, and Broida,¹¹ who find that there is an optimum ratio of O_2/Ba which produces a maximum yield of BaO, as detected by its fluorescence spectrum. A microwave discharge in the oxygen before mixing reduced the BaO fluorescence. Presumably the pro-

(9) W. R. S. Garton, W. H. Parkinson, and E. M. Reeves, *Proc. Phys. Soc.*, **80**, 860 (1962).

(10) (a) A. Gallagher, private communication, June 1969; (b) A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1968.

(11) K. Sakurai, S. E. Johnson, and H. P. Broida, *J. Chem. Phys.*, **52**, 1625 (1970).

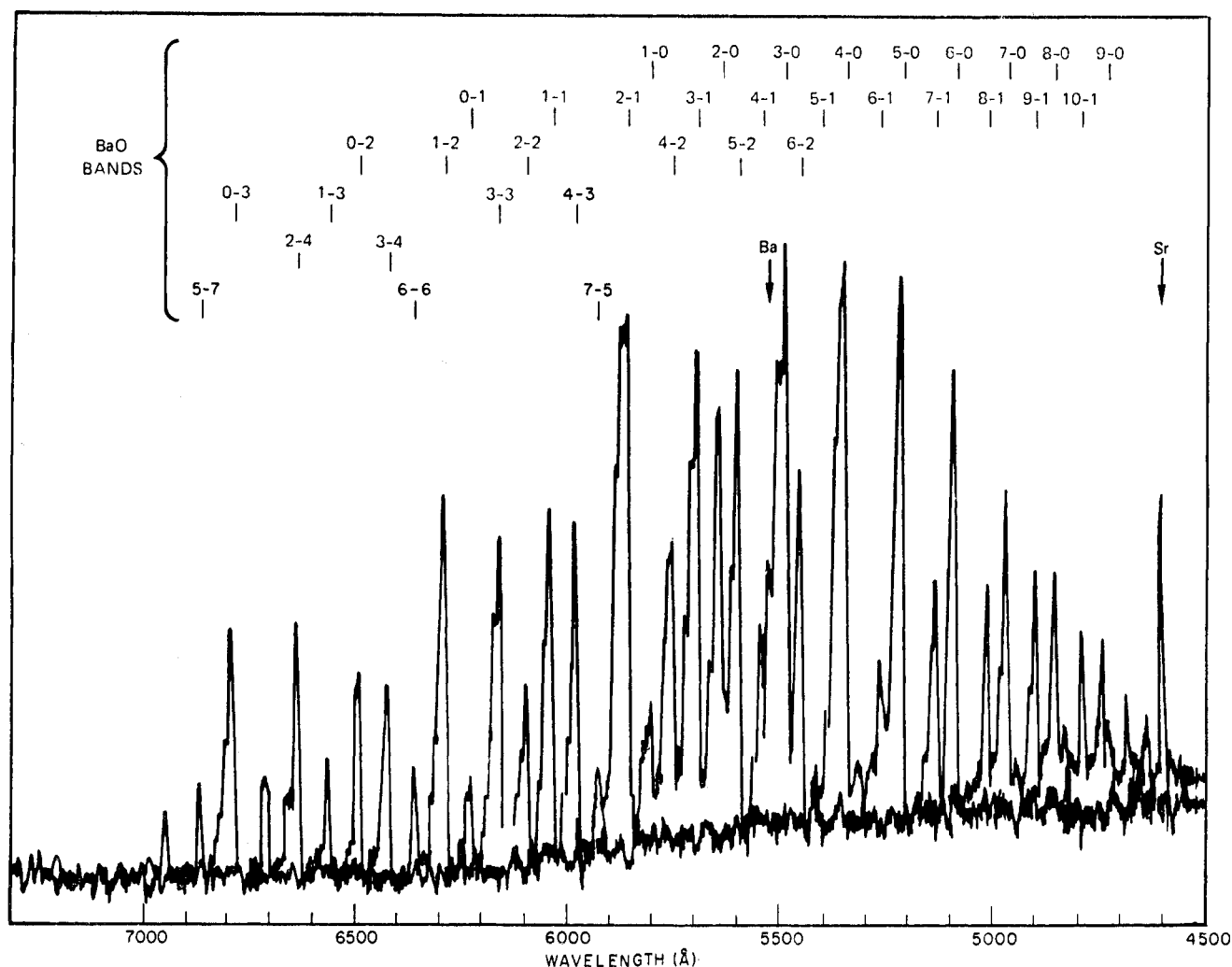


Figure 4. BaO spectrum obtained from release at 106 km.

duction of a small amount of atomic oxygen was accompanied by a corresponding reduction in the O_2 density. They favor the view that an excessive increase in the amount of O_2 present quenches the $A^1\Sigma$ state of BaO. However in upper atmosphere releases at 100 km the BaO fluorescence is strongly extinguished, yet the time between collisions (0.4 msec) is much longer than the measured lifetime of the excited state (12 μ sec). Therefore absence of BaO fluorescence at 100 km is attributed to a lack of BaO. A mass spectrometric study of species present in the barium-oxygen system¹² showed no reaction of BaO with O_2 , and no Ba-O species in which the ratio O/Ba was greater than unity were observed. Possibly the high temperature or the ionizing beam prevent such species from being observed.

One curious feature of the ultraviolet-screened experiments already referred to was the slow observed rate of disappearance of the low neutral barium clouds which could only be explained by assuming a rate of oxidation some ten times slower than for releases in full sunlight. With the data available it cannot be

determined whether the boundary between slow oxidation and normal oxidation depends on altitude or screening height. No major change in atmospheric composition at twilight exists which can be invoked to explain this phenomenon. The experiment is to be repeated with simultaneous rocket-borne measurements of the solar uv irradiation at selected wavelengths.

Other Observed Reactions

The foregoing three reactions are accompanied or followed by other reactions which are only significant under certain conditions. We shall discuss each of these separately below.

(a) *Recombination.* At the electron temperatures found in the upper atmosphere, radiative recombination has been shown to be much more significant than dielectronic recombination.¹³ The rate coefficient for

(12) M. G. Inghram, W. A. Chupka, and R. F. Porter, *J. Chem. Phys.*, **23**, 2159 (1955).

(13) L. Goldberg, "Autoionization," A. Temkin, Ed., Baltimore, Md., 1966, p 14.

radiative recombination of barium ions is probably about $10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ so that a plasma density as large as 10^7 cm^{-3} would have a half-life of 10^5 sec . Thus recombination is negligible at high altitudes and the ultimate disappearance of the ion cloud is due to diffusion. At lower altitudes, other reactions play some role.

(b) *Photodissociation*. Following the release of larger payloads it is noticed that after the ion and neutral clouds have separated there is a much weaker ion "bridge" joining the neutral and ionized clouds. This is believed to be due to photodissociation of BaO to form fresh neutral barium atoms which are again subject to the competing processes of ionization and oxidation. The bridge is due to the ions created from these neutrals. Most of the spectral features of the neutral barium atom have been weakly detected in the "oxide clouds". The photodissociation threshold for BaO is 2637 \AA and this process is considered much more probable than photoionization ($\lambda \leq 2100 \text{ \AA}$). In the ultraviolet-screened experiments an ion bridge did not form. A time constant for photodissociation of a few thousand seconds would permit a detectable ion bridge to be formed without significantly depleting the barium oxide cloud.

(c) *Subsequent Consumption of Barium Oxide*. The barium ion actually constitutes a minor constituent in the ambient neutral atmosphere. For example at 200 km altitude a Ba ion density of $10^7/\text{cm}^3$ is about the highest achieved (and is much higher than ambient ion density of $5 \cdot 10^5/\text{cm}^3$) yet is only $1/1000$ of the local neutral ambient density. Even the local O_2 number density at this altitude is about 40 times as great as the barium ion density, so appreciable depletion of O_2 should not be observed. On the other hand, at altitudes near 100 km, the expanding barium vapor release actually pushes the ambient atmosphere aside and it is therefore possible to produce a photoionized core before the ambient O_2 molecules reach the center. In recent releases performed in the 100-km region, persistent ionization with a density of $4 \times 10^6 \text{ cm}^{-3}$ was detected by radiofrequency techniques. Optical detection of ions was unsuccessful using conventional techniques due to the bright sky background at the release conditions necessary for photoionization and because of the dense barium oxide cloud which was generated. The barium oxide bands scatter efficiently throughout the visible spectrum (see Figure 4) and ion and neutral clouds do not separate at these altitudes.

Spectroscopic observations of these 100-km region releases showed that BaO itself may be consumed. At altitudes below 100 km the BaO disappeared within 1 sec to a cloud of white smoke. At 107 km the BaO cloud intensity reached a peak within 1 or 2 sec of release and then decayed over 20 sec.

These releases have yielded many spectra of the BaO band system and over 40 bands have been identified, almost filling the Deslandres table out to $v' = 10$ by

$v'' = 4$. Peak intensities appear to follow closely the first three Condon parabolaes.¹⁴ These releases may prove to be useful sources of oxide band spectra where relative intensity data will yield information concerning the variation with internuclear distance of the electronic transition moment. In laboratory spectra such measurements may be rendered inaccurate due to the intense electric fields of the exciting arc or other aspects of the excitation mechanism. Information concerning the absolute oscillator strength of the $A'\Sigma-X'\Sigma$ transition may also be derived from spectroscopic data on releases in the 150–200-km range.

As has already been pointed out, strontium has no metastable levels and neither oxidizes nor ionizes to any significant extent compared with barium at high altitudes. There is, however, some evidence that strontium is slowly consumed at 108 km, and at 98 km the strontium decays as rapidly as the barium.

Concluding Remarks

Many of the processes leading to the generation of an ionized plasma following a release of barium vapor are now well understood. There are many other associated mechanisms which become important under certain conditions, and which are yet to be completely documented. The present state of our knowledge concerning barium releases may be summarized by Figure 5. The major limitation to barium yield in the

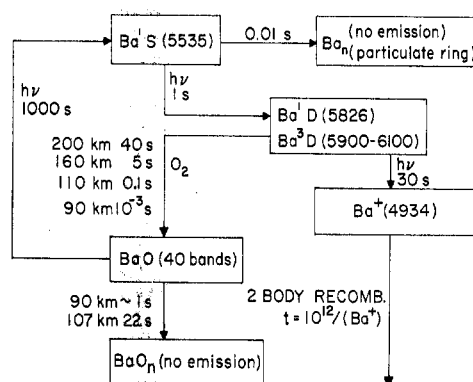


Figure 5. Diagram showing overall state of knowledge of processes involved in upper atmospheric barium releases.

thermite reaction mixture is that 80–90% of the "free" barium is trapped in the solidifying droplets expelled from the canister and significant increases in release temperature are limited by materials used. The use of larger payloads will not give a corresponding increase in ion density since optical thickness effects limit the rate of production of metastable barium.

(14) W. M. Vaidya, D. D. Desai, and R. G. Bidaye, *J. Quant. Spectrosc. Radiat. Transfer*, **4**, 353 (1964).

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Difference Chromatography of Sea Water¹

by Paul C. Mangelsdorf, Jr.,*

Department of Physics, Swarthmore College, Swarthmore, Pennsylvania 19081

and T. Roger S. Wilson

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543 (Received January 11, 1971)

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When sea water samples are analyzed by the method of difference chromatography the composition differences are resolved into the coherent waves described by Helfferich and Klein. The predicted sequence of affinity cuts is found. Cation composition variations produced in the initial anion front by changes in total normality are found to be satisfactorily predicted by the theory. Similar variations produced by changes in the SO_4/Cl ratio are found to be consistent with the theory and with previously verified consequences of a sea water model due to Garrels and Thompson. However the activity coefficient of K^+ is more strongly reduced by SO_4^{2-} enrichment than the model predicts.

Introduction

Sea water is a concentrated mixed electrolyte solution containing large proportions of ions of certain lithophilic elements² plus trace amounts of everything else that can be leached from a planetary surface. The specific composition of sea water is of theoretical interest only to geochemists. To the physical chemist sea water represents one instance of a large class of possible mixed electrolyte solutions, therefore of practical interest only because there is so much of it.³

The constancy of the relative proportions of the major ions in sea water has long been recognized,⁴ and has been amply verified by the recent work of Morris and Riley,⁵ Culkin and Cox,⁶ and Riley and Tongudai,⁷ summarized in Table I.

The reported variations in ionic proportions are small and not very systematic. However, all the geochemical factors controlling the composition of sea water must be reflected in such small residual variations from place to place and from time to time.

At Woods Hole we have been attempting to study these variations by the use of "difference chromatography,"⁸ a form of ion-exchange chromatography in which a sample of an unknown mixture is injected into a carrier stream of a standard mixture closely similar to the unknown. The method is a null method: if the mixtures are identical a detector at the column output will give a steady undeflected reading. When compo-

sition differences do exist between the two mixtures these are resolved into a set of "coherent" composition pulses,⁹ eigenvectors in composition space,⁸ each of which travels separately down the column at a characteristic speed. The theory of such coherent pulses and steps has been fully developed in the recent definitive volume by Helfferich and Klein.⁹

It should be strongly emphasized that the response pattern obtained is *not* (as might have been expected) one in which each component has its own separate pulse or step across which the concentrations of all other components are constant. On the contrary the concentrations of *all* sorbed components will, in general, change during each pulse or step.

(1) Contribution No. 2623 from the Woods Hole Oceanographic Institution.

(2) V. M. Goldschmidt, "Geochemistry," A. Muir, Ed., Oxford University Press, 1954, Chapter II, Table VI.

(3) About 1.37×10^{21} l., all told: H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, "The Oceans," Prentice-Hall, Englewood Cliffs, N. J., 1942, Table 4.

(4) J. P. Riley in "Chemical Oceanography," Vol. 1, J. P. Riley and G. Skirrow, Ed., Academic Press, New York, N. Y., 1965, Chapter I, Historical Introduction.

(5) A. W. Morris and J. P. Riley, *Deep-Sea Res.*, **13**, 699 (1966).

(6) F. Culkin and R. A. Cox, *ibid.*, **13**, 789 (1966).

(7) J. P. Riley and M. Tongudai, *Chem. Geol.*, **2**, 263 (1967).

(8) P. C. Mangelsdorf, Jr., *Anal. Chem.*, **38**, 1540 (1966).

(9) F. Helfferich and G. Klein, "Multicomponent Chromatography," Marcel Dekker, New York, N. Y., 1970.