Atomic and Molecular Properties of Metals from Artificial Cloud Experiments in the Upper Atmosphere

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Time and frequency resolved observations of metal vapor clouds in the upper atmosphere can be used to obtain information on atomic and molecular properties of the metals involved, e. g. atomic transition probabilities, photoionization cross sections, chemical reactivity of atoms in the ground state and in excited states. Experimental techniques of evaporation, the methods of observation and some of the more important results are discussed for Sr, Ba and Eu, in particular those which cannot be derived by laboratory experiment, namely, radiative transitions and oxidation processes which involve metastable states. Especially one finds that the photoionization and oxidation processes of Eu and Ba are significantly different in contrast to theoretical predictions.

I. Introduction

A well-known tool for the study of ionospheric and magnetospheric phenomena are artificial metal vapour clouds that can be observed using ground-based instrumentation [1]. In addition to the geophysical information obtained, the fluorescence spectra of the clouds provide some insight into processes which are of interest from the viewpoint of atomic and molecular physics: atomic level population in the pure solar radiation field, photoionization processes, reactions between cloud and atmospheric particles (e. g. oxidation). The different behaviour of some metals (especially Ba, Sr and Eu) with similar atomic configuration is discussed in this publication. In particular, we present some information about problems that cannot be investigated in the laboratory, e. g. the lifetime of metastable atoms, the reactivity of metastable atoms or atoms produced by high-velocity vapour jets with atmospheric oxygen.

II. Generation of Metal Vapour Clouds in the Upper Atmosphere

The metal vapour clouds are generated by two major processes [2]:

(i) by partial combustion of the metal in a container, which is carried to altitudes above 120 km. The combustion products (typically 500 g, molar ratio 2.2 Eu: Cu 0 or 1.5 Eu: Ba: Cu 0 for equal yield of Eu vapor) expand through a nozzle into the atmosphere producing 0.3 mole of vapour with an initial velocity of 1.2 km sec^{-1} corresponding to kinetic energies relative to atmospheric particles of 0.1 eV.

(ii) by shaped charges where metal cones are compressed by a solid state shock wave generated by an explosion. The metal is partly evaporated and accelerated to an initial velocity up to 15 km sec^{-1} corresponding to kinetic energies relative to atmospheric particles of up to 20 eV. As shown in Fig. 1 this method provides well-defined distributions over velocities $\dot{x}$ parallel and $\dot{y}$ perpendicular to the jet axis. These distributions can be changed nearly arbitrarily by changing the configuration of the charge for a degree of evaporation between 0.05 and 0.2.

The evaporation is carried out before dawn or after dusk at altitudes which are still reached by the sun's radiation, while the site of observation is already in the earth's shadow. The sun's depression angle must be larger than 10° for the stray light intensity to be sufficiently low. For a depression angle of 15° the uv-shadow of the earth ($\lambda \approx 2000$ Å) occurs at an altitude of 250 km and the observation time is approximately 20 minutes.

III. Principle of Measurement and Elementary Processes

Figure 2 gives typical values for the upper atmosphere's parameters and for the most important processes that can be studied by means of the clouds. Above 300 km the atmosphere is so dilute that interactions between the expanding metal vapour and the atmospheric gases are negligible (number density

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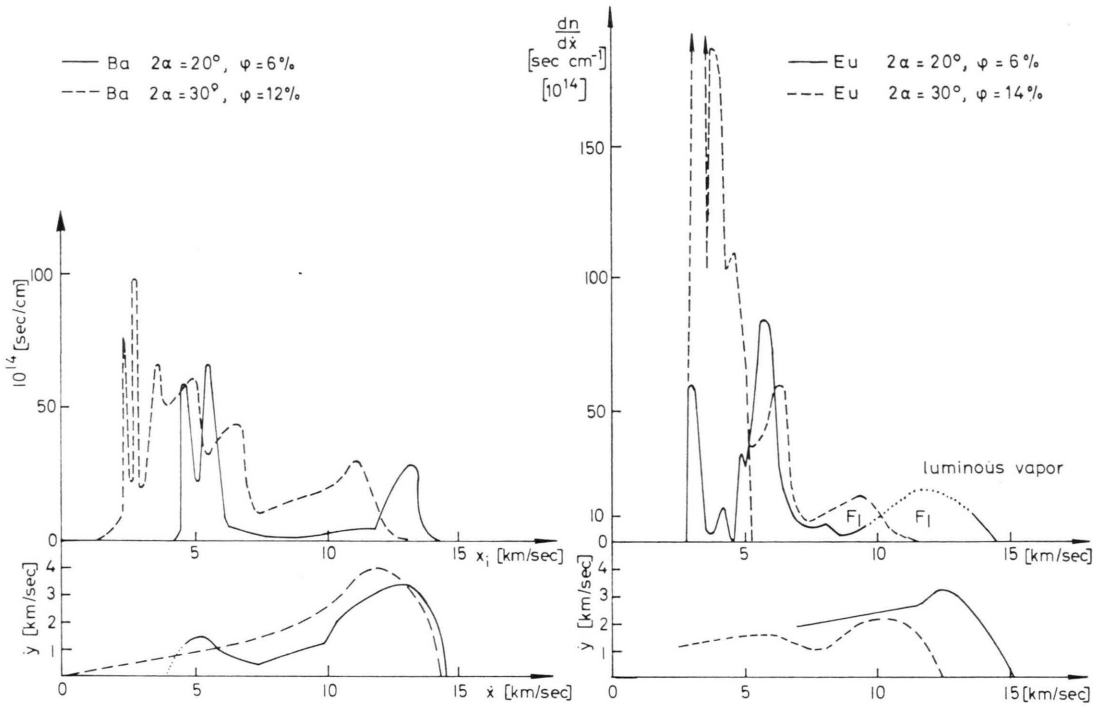

Fig. 1. Generation of vapor jets using shaped charges. Shown is the distribution of vapor velocity $\dot{x}$ parallel and $\dot{y}$ perpendicular to the jet-axis for different cone angles α of the explosive and different degree of evaporation φ.

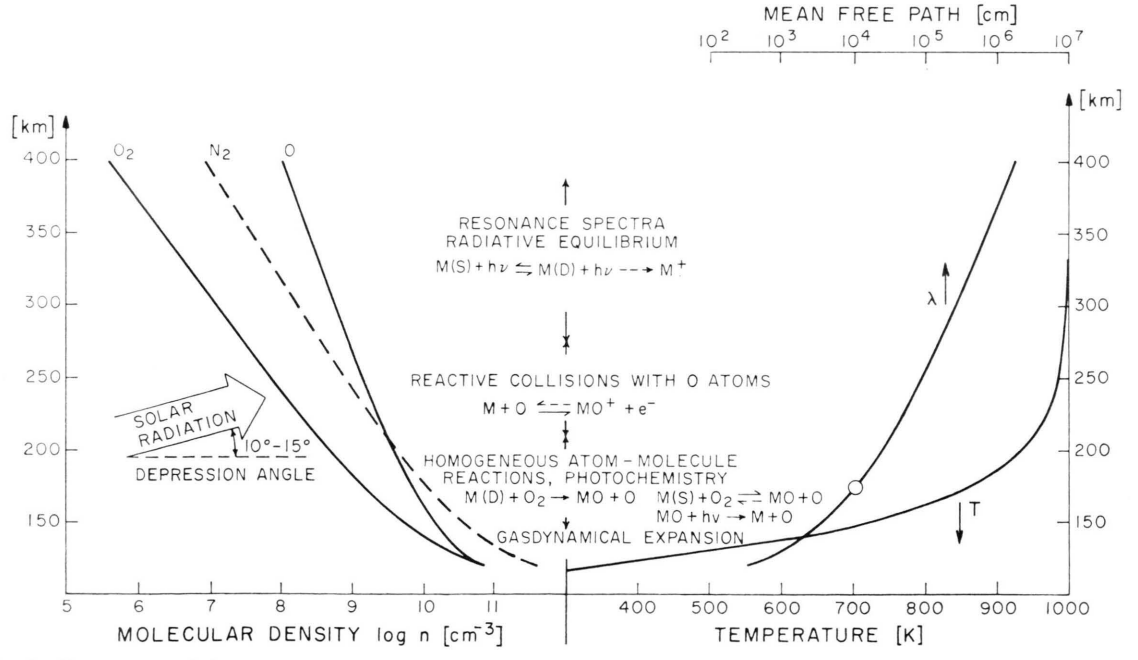

Fig. 2. Parameters of the upper atmosphere and corresponding elementary processes which can be studied by spectroscopy of artificial metal vapour clouds.

$n \sim 10^9\,\mathrm{cm}^{-3}$, mean free path $\lambda \sim 1\,\mathrm{km}$). In this region one observes pure resonance spectra of the cloud atoms. Also metastable levels are populated due to optical pumping by the sun's radiation. At altitudes above 200 km atomic oxygen is the most prominent constituent of the atmosphere. Reactive collisions can occur only by certain direct processes, for example the associative ionization (e. g. for U) as indicated in the figure. In vapour jets even endothermal reactions of this type are possible [2b], but the molecular ion will disappear because of dissociative recombination (electron density $10^5\,\mathrm{cm}^{-3}$). Below 200 km reactions involving molecular oxygen may occur. However, the concentration of atomic oxygen is still high enough for the oxidation to be reversed provided the rate constant for the reverse reaction is sufficiently high. By measuring the rate of molecule formation photometrically one obtains the reaction cross section. One can also measure the corresponding cross sections for the metastable levels, which have been populated by pumping mechanisms. This is a special advantage of the method and allows the reactivity of the same atom in the ground and in the metastable level to be compared. In addition to the chemical reactions the photodissociation of the metal oxide has to be taken into account. Below 150 km the mean free path is very short and the metal vapour cannot mix into the atmosphere without perturbing it appreciably. The observation of this gas dynamical expansion provides no information on elementary processes. Furthermore, the observation time becomes so short that the evolution of the cloud cannot be recorded accurately.

IV. Observational Equipment

The experimental equipment (constructed for use on unprotected sites and under extreme climatic conditions) includes

(i) grating spectrograph with fast objective ($f/0.75$), electrostatical image amplifier (S-20-photocathode) and smear film. Time resolution 1 sec, dispersion 190 Å/mm, accuracy of line position ± 10 Å, field of view $0.1^\circ \times 5^\circ$ ($f = 305$ mm, slit 0.5×27 mm). This instrument gives reasonable fluorescence spectra for stray light intensities corresponding to a depression angle of the sun of 10°.

(ii) 6-channel-photometer with filters of 40 Å band width (FWHM). The light intensity is recorded on magnetic tape by a pulse counting method. Counting rates up to 200 kHz are possible for linear registration. The contribution of the source can be separated from that of the background by observing the source, then the sky without the source and repeating this process periodically. The effective time resolution is $^1/_{10}$ sec. The field of view ($\sim 5^\circ$) is large enough to cover the whole cloud in most cases (cloud diameter 10 – 50 km, diffusion coeffi-caent $D = 2.10^8 - 2.10^{10}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$ at 160 – 250 km altitude [3]).

For geophysical investigations the separation of the neutral particles and ions in the cloud caused by electric fields and atmospheric winds is recorded by normal photographic cameras ($f/2.5$ or $f/1.7$ with 70 mm film, Kodak 2475).

V. Experimental Results and Interpretation

Experiments using alkaline earth elements (Sr, Ba) have been reported in previous publications [3–5]. In the following the results of europium experiments will be presented as well as a comparison of the behavior of all three elements.

a) Behavior of Europium

Spectra of Eu-clouds, which have been generated by the two above mentioned methods of evaporation are displayed in Figure 3. The dominant features in all of these spectra are the strong resonance lines of Eu I (see for comparison the simplified energy level diagram in Figure 4):

$$4f^7\,6s^2\,a\,{}^8S_{7/2}{}^0 \rightarrow 4f^7\,6s\,6p\,y\,{}^8P_{5/2}\ 4661.88\ \text{Å}$$
$$y\,{}^8P_{7/2}\ 4627.22\ \text{Å}$$
$$y\,{}^8P_{9/2}\ 4594.03\ \text{Å}.$$

Furthermore, some lines belonging to transitions from the S-ground level with gf-values below 0.1 are clearly seen. The recorded intensity ratios correspond to values of the oscillator-strengths quoted in the literature [6]. In contrast to the Ba-spectra the Eu-spectrum shows no lines belonging to transitions from metastable levels, although the electron configuration is quite similar. An upper limit for the intensity of the strongest of those lines is given by the intensity I_m of the weakest line identified in the Eu spectrum:

$$I\,(6266.95\ \text{Å})_m = u\,B \cdot n_s < 10^{-2}\,n_s\ \text{photons}\ \mathrm{sec}^{-1}$$

where u, B and n_s denote energy density of solar radiation, Einstein absorption probability and number of Eu-atoms in the ground state respectively.

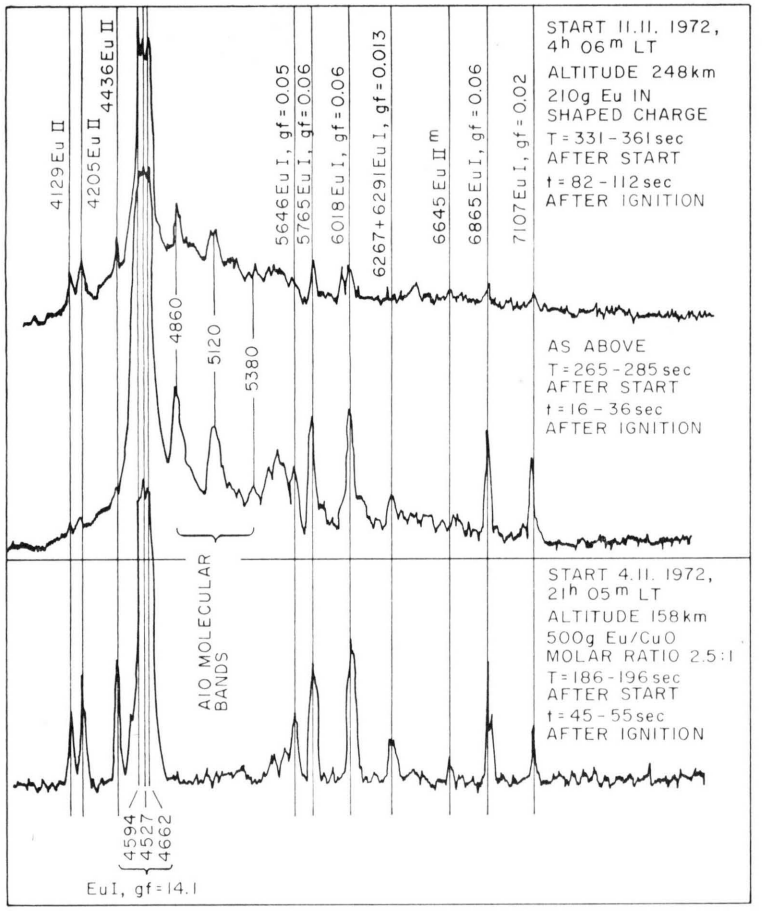

Fig. 3. Examples of spectra of europium clouds generated in the upper atmosphere.

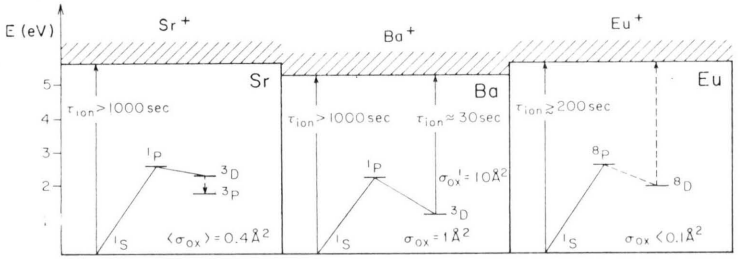

Fig. 6. Comparison of the behavior (photoionization, oxidation) of elements with similar electronic structure (Sr, Ba, Eu) in cloud experiments. τ_{ion} is the time scale for photoionization in the sun's radiation

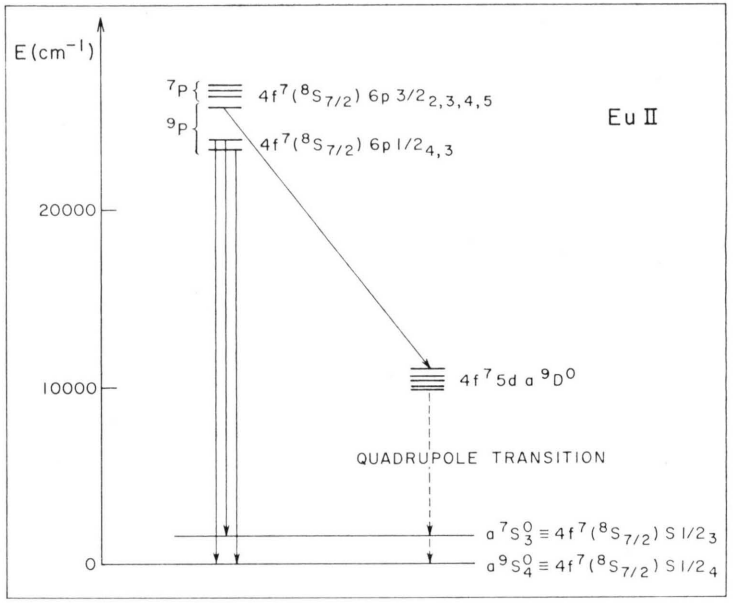

Fig. 4. Simplified energy level diagram of Eu I. Observed spectral lines are indicated by full lines. Transitions which are assumed to occur at a fairly low rate are shown by dashed lines.

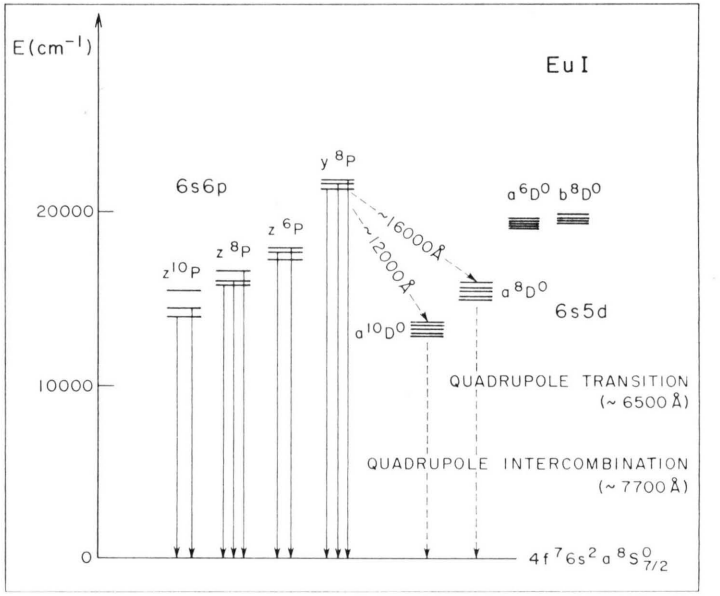

Fig. 5. Simplified energy level diagram of Eu II. Spectral lines shown

Since transition probabilities for non-resonance lines of Eu are poorly or not at all known, it seems to be useful to infer some general limits from these measurements by simple estimates.

Considering photoionization as a perturbation, the ratio of the *steady state population* of the D and S states can be calculated for a three-level atom, since the interaction among all the metastable D-states is faster than the interaction between them and the ground state. In the optically thin case and assuming collisions are negligible one has

$$n_D(A_{DS}+u_{DP}B_{DP}) = n_S u_{SD} B_{SD} + n_P A_{PD},$$
$$n_P(A_{PS}+A_{PD}) = n_S u_{SP} B_{SP} + n_D u_{DP} B_{DP}.$$

Obviously, for $A_{PS} \gg A_{PD}$ (since $A \sim 1/\lambda^3$) and $u_{SD} B_{SD} \approx 0$ (metastable states) one obtains

$$\frac{n_D}{n_S} = \frac{A_{PD} u_{SP} B_{SP}}{A_{PS}(A_{DS}+u_{DP}B_{DP})}.$$

Using experimental values [6] for the transition probabilities and the energy density of the solar radiation field outside the earth's atmosphere one obtains

$$n_D = 0.87 \frac{g_D f_{DP} \cdot n_S}{g_S(A_{DS}+34.\, f_{DP})}$$

where f is the oscillator strength.

Since even the strongest line ($a\,^8D_{11/2} - z\,^8F_{13/2}$, $\lambda = 5992.83$ Å, $f = 0.18$ [7]) of octet transitions from the metastable states is not observed, one has for each of these transitions

$$(u\,B)_{DF} \cdot n_D < I_m = 10^{-2} n_S.$$

Also since no quadrupole lines ($\lambda \approx 6500$ Å) are observed one has

$$n_D \cdot A_{DS} < I_m.$$

These equations provide upper limits for the oscillator strengths of the P – D transitions and estimates of the quadrupole transition probabilities of the D states

$$f_{DP} < 10^{-2},$$
$$A_{DS} \approx 1.2\ \mathrm{sec}^{-1} \text{ (if } f_{DP} \approx 10^{-2}).\ *$$

* As has been found recently the f-value for one of the corresponding transitions in barium is (E. Trefftz, personal communication 1973)

$$f(6^1P - 5^1D) \approx 10^{-3}$$

so that optical pumping occurs via high-lying P-levels (7P, 8P).

Intercombination lines $^8P - {}^{10}D$ seem to be even weaker, since the extremely strong line $a\,^{10}D_{13/2} - z\,^{10}F_{15/2}$ $\lambda = 5830.98$ Å is not observed.

A somewhat different behavior is shown by the spectrum of Eu II. Here, in addition to transitions from the ground state (for a simplified energy level diagram see Fig. 5)

$$4f^7\,6s\,a\,^9S_4^0 \rightarrow 4f^7\,6p\,z\,^9P_4 \quad 4129.73\ \text{Å}$$
$$\rightarrow \quad z\,^9P_3 \quad 4205.05\ \text{Å}$$

also transitions from metastable states are observed

$$4f^7\,6s\,a\,^7S_3^0 \rightarrow 4f^7\,6p\,z\,^9P_4 \quad 4435.58\ \text{Å}$$
$$5d\,a\,^9D_6^0 \rightarrow \quad z\,^9P_5 \quad 6645.11\ \text{Å}.$$

The f-values estimated from the intensities of the strongest lines are around 0.1 and in fairly good agreement with available laboratory measurements [7a]. They can be calculated quite accurately by central-field-methods as for ionized barium. The energy dependence of the levels and especially the intensity ratio of the two lines being emitted from the same upper state ($^9P_4$) indicate that the P-state of Eu II is described by J_0 j-coupling rather than by LS-coupling.

From the decrease of the luminosity of the neutral Eu cloud with time one obtains for the ionization time constant in the solar radiation field [7b] $\tau_{ion} \approx 200$ sec (e-folding time).

b) Comparison of the Elements Sr, Ba, Eu

1. Photoionization

All three elements possess a very similar electronic structure, e. g. for the ground state

$$\text{Sr I: } 5s^2\,^1S_0, \quad \text{Ba I: } 6s^2\,^1S_0,$$
$$\text{Eu I: } 6s^2\,^8S_{7/2}^0$$

and metastable D-states could in principle be populated by optical pumping mechanism.

The population of D-levels for the different elements will now be estimated using the results of the previous subsection (formula for level-populations). For barium

$$u_{DP} B_{DP}/A_{DS} > 1$$

and one obtains for the total number N_D of atoms in all D-states with total statistical weight G_D

$$\frac{N_D}{N_S} = \frac{G_D}{G_S} < \frac{u_{SP}}{u_{DP}} \left(\frac{\lambda_{SP}}{\lambda_{DP}}\right)^3 > \approx \frac{G_D}{G_S} e^{-\langle h\nu_{DS}\rangle / kT_S}$$

where in the derivation of the last term Wien's law (with a solar temperature T_S) has been used for

simplicity to show the relationship with a Boltzmann distribution. For barium one has

$$N_D/N_S \approx 1 .$$

Measurements [8] and more detailed calculations [4] confirm this result. For europium the above estimates (Section a) give

$$u_{DP} B_{DP}/A_{DS} \lessapprox 0.3$$

which differs greatly from the theoretical prediction. Using this condition one obtains after some manipulation

$$\frac{N_D}{N_S} \approx \left(\frac{u_{DP} B_{DP}}{A_{DS}} \right) \frac{G_D}{G_S} e^{-\langle h\nu_{DS} \rangle / kT_S} .$$

For the octet-states one has

$$N_D/N_S \lessapprox 10^{-2} .$$

For strontium the emission probabilities A for direct (^{3}D) or indirect (^{1}D) transitions are nearly of the same order of magnitude as those for the P-states. Therefore

$$\frac{N_D}{N_S} = \frac{A_{PD} \dfrac{G_P}{G_S} W e^{-\langle h\nu \rangle / kT_S}}{A_{DS} + \dfrac{G_P}{G_D} W A_{PD} e^{-\langle h\nu \rangle / kT_S}} \approx W \frac{G_P}{G_S} e^{-\langle h\nu \rangle / kT_S}$$

where W is the dilution factor of the sun's radiation

$$W \sim R^2/4 r^2 = 6 \cdot 10^{-6}$$

with R the solar radius and r the mean sun-earth distance.

The results are summarized in Figure 6. Photoionization of barium occurs out of the metastable levels, where the effective cross section has approximately the same value as for the ground state [9] but the solar radiation field is more intense by a factor of 30. For Sr the photoionization can only occur out of the ground state, so that the time constant τ_{ion} is very long. For Eu the photoionization occurs also essentially out of the ground state but the corresponding cross section should be higher than for Ba (see τ_{ion} in Fig. 6 for comparison). This is to be expected, since for europium the ionization is characterized by transitions in a two-electron spectrum as for Ba

$$4f^7\, 6s^2 \rightarrow 4f^7\, 6s\, np \quad \Delta l = 1 ,$$
$$4f^7\, 6s^2 \rightarrow 4f^7\, 5d\, np' \quad \Delta l = 2 \text{ (autoionization)}$$

but in addition very intense transitions can occur by two-electron transitions to a configuration with $4f^6(^7F)$ as a parent term

$$4f^7\, 6s^2 \rightarrow 4f^6\, 5d^2\, ns .$$

The measured intensity [10] ratio between these groups of lines is 1:4 (see Fig. 7) so that the measured τ_{ion} can be explained by these arguments.

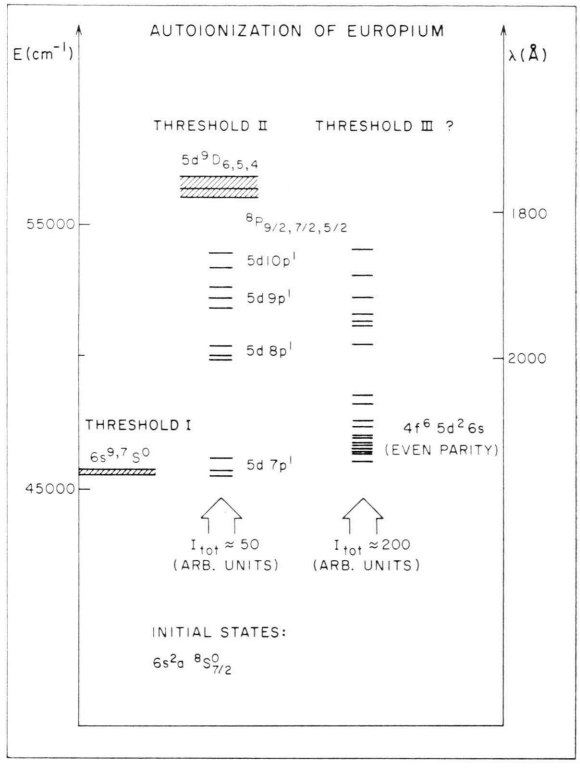

Fig. 7. Relative intensities of autoionizing transitions in Eu I corresponding to different electronic configurations. The autoionization transitions of Ba I correspond to the transitions shown on the left part of the figure.

As a practical consequence Ba is most suitable for geophysical experiments, which require fast photoionization, such as ion jets. Good visibility of the jet between magnetically conjugate points, or to high altitudes in experiments at high magnetic latitude, is afforded by fast ionization [2b]. Eu, however, is more suited for studies of the outer magnetosphere. Fast ionization would involve high pressure and hence strong perturbation of the medium to be studied.

2. *Oxidation*

The oxidation of the element M according to the exchange reaction

$$M + O_2 \rightarrow MO + O$$

will now be discussed. Although the formation rate constant should be high enough, strontium oxide is not formed under the conditions in the upper atmo-

sphere, because the exchange reaction is endothermal [5]. For barium the reaction cross sections for the formation of oxide out of the ground state have been measured [5] and BaO has been observed. This will be discussed in the following paragraph. One would also expect that Eu atoms form oxides out of the ground state with typical time scales of the order of 60 sec at 160 km altitude, if the corresponding cross section for Ba ($\sigma = 1$ Å^2) is adopted. Moreover, the partial equilibrium should be in favor for EuO (EuO/Eu $= 7 \cdot 10^2$), since the reaction is endothermal ($\Delta E = 0.7$ eV [11]). However, no EuO is observed in the cloud experiments. The reason for this negative result could in principle also be explained by a low value for the oscillator-strength of EuO. But in this case the amount of neutral europium would decrease due to photoionization and oxidation, where the contribution of the second process depends on the O_2 density, i. e. the altitude of the clouds. Since this dependence of altitude is not observed in the decrease of the luminosity of the neutral cloud, no appreciable amount of EuO can have been formed. On the basis of the present knowledge of the thermochemistry and reaction behavior of similar systems, this negative result is not understood at all.

The observations of Ba show results that have not been obtained in the laboratory so far. The observed rate constant for the formation of oxide at about 1000 °K is $K_{ox} = 10^{-10}$ cm^3 sec^{-1}. Since the atoms are partly in the ground state (with $\sigma_{ox} = 1$ Å^2, see above) and partly in the metastable states (σ'_{ox}) one has for a thermal velocity $\langle v(T) \rangle = 10^5$ cm sec^{-1}

$$K_{ox} = (\sigma_{ox}' N_D / N_S + \sigma_{ox}) \langle v \rangle .$$

Using the above values for the steady state population one obtains

$$\sigma_{ox}' = 10 \text{ Å}^2 .$$

Triplet states of BaO need not be considered here, because the a^3II state has been found to lie about 2.2 eV above the ground state [12]. Hence it is energetically not accessible in these reactions.

One can try to derive the above cross section using a simple electron-jump model [13] for processes adiabatic with respect to electronic transitions and without repulsive forces. The attractive forces are assumed to be isotropic and given by the Coulomb law (usually without corrections for ion polarizability) of the ion pair $Ba^+O_2^-$. For infinite distance of these ions their energy is above that of the reactants Ba and O_2 by the amount $I_p - E_A$, where I_p is the ionization potential of the metal and E_A the electron affinity of the oxygen molecule (Figure 8). The electron jump occurs at $r = r_c$, where the potential energy curve of the ion pair crosses that of the reactants

$$r_c = \frac{e^2}{I_p - E_A} \quad \text{with} \quad \sigma_{ox} = \pi r_c^2 .$$

One obtains $\sigma_{ox} = 29$ Å^2 and $\sigma_{ox}' = 48$ Å^2 for the oxidation of atoms in the ground and lowest metastable states, respectively, with corresponding parameters $r_c = 3$ Å and $r_c' = 4$ Å. For reactions out of the ground state exchange forces obviously impose strong constraints on the geometric orientation and large deviations from Coulomb's law occur. The relatively low cross section, especially since the reaction has no measurable activation energy, seems to be a selection effect in favor of those collisions where the reactants have the right relative orientation. Because of the lower ionization potential (1.2 eV) the distance r_c' between metastable Ba and O_2 is larger and obviously the 5d orbitals do not extend beyond this region. These orbitals seem to be less extended than S-orbitals as can be seen from the

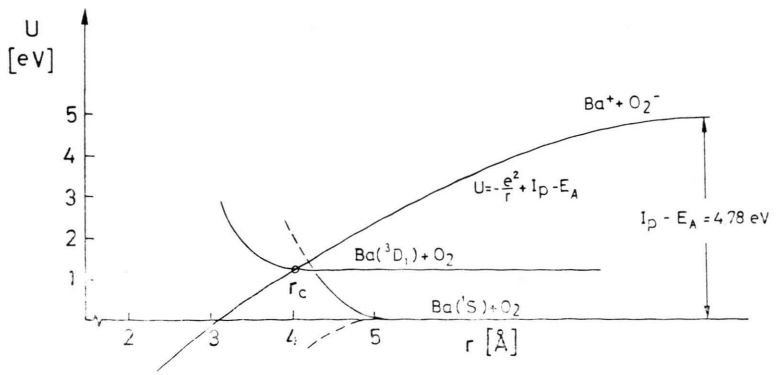

Fig. 8. Application of the electron-jump model to the excitation of barium out of the ground state and out of metastable states. I_p is the ionization potential of Ba and E_A the electron affinity of O_2.

temperature dependence of inelastic collision with rare gas atoms [14]. Thus the electron-jump model is a better description of the reactive cross section the higher the total internal energy of the colliding particles.

VI. Summary

Artificial metal vapour clouds in the upper atmosphere, which have successfully been used for the study of ionospheric and magnetospheric phenomena, can at the same time provide some information about the atomic and molecular properties of the metals involved. Thus, for Sr, Ba, and Eu estimates or limiting values are derived for some of the following quantities: transition probabilities of non-resonance lines (e. g. $y\,^8\mathrm{P} - a\,^8\mathrm{D}^0$ transitions in Eu I), lifetime of metastable states (e. g. $5\mathrm{d}^{3,1}\mathrm{D}$ in Ba I, $5\mathrm{d}\,^8\mathrm{D}^0$ in Eu I), photoionization cross sections (ground state ionization cross section of Eu I $\sigma \approx 5 \cdot 10^{-17}$ cm^2 in the wavelength range $\lambda = 2050$–2200 Å as compared to $\sigma \approx 10^{-17}$ cm^2 in the range $\lambda = 2100 - 2400$ Å for Ba I, check of theoretical results for the photoionization cross section of Ba I out of metastable levels), oxidation cross section for atoms in the ground state ($\sigma_{OX} < 0.1$ Å^2 for Eu I as compared to $\sigma_{OX} = 1$ Å^2 for Ba I) and for atoms in the metastable state ($\sigma_{OX}' = 10$ Å^2 for Ba). The principal difference between cross sections out of ground states and out of metastable states can be discussed using a simple electron jump model. The transition probabilities for Eu II resonance lines which are estimated from the experiment are in fairly good agreement with the results of laboratory measurements and central field calculations which have been considered uncertain so far. This result is important for the treatment of cool peculiar A stars. On the basis of their similar thermodynamical data, optical properties [15], and electron structure, one would expect similar photoionization and oxidation processes to occur for Ba and Eu, whereas the given experimental results differ greatly from this theoretical prediction.

Acknowledgments

Some of these experiments, especially those with europium would not have been achieved without the enthusiastic work of Dr. A. Valenzuela and the activity of his coworkers from CNIE, Argentina. We also gratefully acknowledge H. Föppl, H. Hippmann and W. Lieb, who were involved in the construction of observational equipment as well as in the campaign itself. A. Fritsch developed with great skill a method for fabrication of Eu-lines in shaped charges.

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