Holmium Atoms and Small Clusters in Inert Matrices

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The UV−vis spectra of holmium atoms isolated in argon and krypton matrices at 9 K have been studied in the 200−800 nm region. By comparison with gas phase data it is possible to separate the multitude of absorptions in the 400 nm region into transitions belonging to holmium atoms in two different sites, only one of which is photostable. Prolonged irradiation of dilute Ho/Ar matrices results in the simultaneous growth of two new doublets at 498/504 and 558/562 nm, attributed to the holmium dimer Ho_2. Cocondensation of holmium atoms with argon at temperatures above 10 K results in gradual breakdown of isolation conditions with indications of global clustering. Not even traces of isolated holmium atoms can be observed at deposition temperature above 17 K. Photoactivation permits tentative assignment of bands at 608 and 450 nm to Ho_3 and Ho_4, respectively.

Introduction

Although the lanthanide elements exhibit a very rich and varied coordination and organometallic chemistry,[1−3] so far only a few examples of zero oxidation state complexes have been characterized.[2] Most complexes of interest are prepared by metal atom cocondensation with prospective ligands, and thus information on the ground and excited states of lanthanide metal atoms and small clusters is highly desirable. Gingerich[4] estimated in 1980 the bond strength in homonuclear and bimetallic lanthanide dimers using mass spectroscopy, but there is no doubt that refined data are needed, especially when considering the decisive, but still uncertain, influence of lanthanide elements in modern high-temperature superconductors.

Little is known even about such basic properties as the optical spectra and reactivity of lanthanide atoms, small clusters, and monoxides. We have started to survey the characteristics of these species using matrix isolation and optical detection techniques. In a first step we described the cocondensation and photochemical reactions of samarium atoms in inert and reactive matrices.[5] As already indicated in a preliminary communication,[6] we noticed an even more fascinating picture in our studies on holmium, which are now reported in detail below.

Some 30 years ago the gas-phase emission spectra of rare earth elements were studied, and most of the transitions observed have been assigned.[7,8] As, by comparison with the d-block elements, the lanthanide metals are expensive, sensitive to air exposure, and exhibit a multitude of transitions, only a few matrix isolation spectroscopic studies[9−12] have been performed, and even those are often incomplete and/or lack assignments. For example, phonon sidebands in the optical absorption spectrum of Eu and Sm atoms isolated in inert matrices have been investigated[13,14] over a range of 30 nm. The optical spectra of ytterbium[15,16] and thulium[17] atoms have been assigned; for Yb_2 in Ar and Kr matrices an extensive vibrational structure around 550 nm with a spacing of 48 cm^{-1} was reported.[16] This transition was assigned to $6s^2(^1S_0)(^1\Sigma_g^+) \rightarrow 6s6p(^1P_1)(^1\Sigma_u^+)$, in agreement with the similar spectra found for Ca_2 and Mg_2, which are held by weak van der Waals forces in the ground state.[18,19]

Dimers of all lanthanide elements with $4f^n6s^2$ configurations are expected to exhibit similar spectra, as the inner 4f-electrons supposedly are not involved in bonding. This was confirmed for the closed f-shell ytterbium with a $4f^{14}6s^2(^1S_0)$ ground state.[16] Interestingly, a recent ESR study of Gd_2 indicated[20] the presence of 18 unpaired spins (including the 14 inner-shell 4f-electrons), which would make the electronic ground state a fascinating $^{19}\Sigma$, the highest spin multiplicity ever reported for a diatomic molecule. This makes it even more important to obtain spectroscopic information on lanthanide dimers with partially filled 4f-orbitals, with the hope of gaining insight into the electronic structure and bonding in these molecules.

Of the diatomic lanthanide molecules it seems that so far the monoxides, which exhibit extremely complex absorption spectra, have found the most attention, both theoretically[21] and experimentally.[22−25] Turning to the case of holmium, a sequence of bands observed in the gas phase was attributed by Gatterer[22] to HoO, high-resolution spectra were obtained by Kaledin,[23] and the electronic, vibrational, rotational, and hyperfine structure of gas-phase HoO has been examined by a laser spectroscopic technique.[24] As we will show later, the only matrix isolation study[25] of the optical spectra of lanthanide monoxides in inert gases clearly needed to be clarified.

Materials and Methods

The matrix-isolation setup, with quartz crystal microbalance to control the metal sublimation rate and with characterization of the products by infrared and UV−vis spectroscopy on the same window, has been described previously.[26,27] As a recent improvement it is now possible to obtain emission and excitation spectra from this window, too. Holmium metal (Goodfellow, 99.9%) and holmium(III) oxide powder (Alfa, specpure, t.m.i. 110 ppm) were resistively evaporated from tantalum Knudsen cells and cocondensed with matrix gases (Messer-Griesheim, Ar 5.7, Kr 4.7) at various concentrations and at deposition temperatures between 9 and 20 K. To secure temperature readings, an extra thermocouple was imbedded into a drilled cavity of the NaCl window.

Electronic spectra in the range 800−200 nm were recorded on a Perkin-Elmer 320 spectrophotometer (resolution 0.5 nm) with PE3600 data station. For near-IR spectra in the 2500−800 nm region a PE330 was used. Routinely the matrices were

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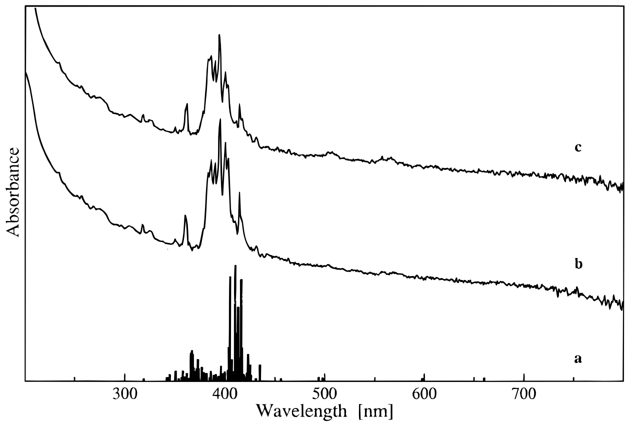

Figure 1. Comparison of (a) the gas-phase emission spectrum of holmium atoms with (b) the UV−vis absorption spectrum of holmium atoms isolated in argon at high dilution (Ho/Ar < 1/10^4) and full cooling (8−9 K); (c) the result of a 10 min narrow-band irradiation at 405 nm.

checked for impurities in the 4000−600 cm^{-1} infrared region with a PE580.

Excitation and fluorescence spectra were taken, for selected experiments, from the same matrix as used for the IR and UV−vis investigations. In the Shimadzu RF5001 PC spectrofluorophotometer employed the excitation and fluorescence collection optics are at 90°, and the light fluxes are dispersed by separate monochromators for the 200−700 nm region. The matrix sample was located at the focal points of the collection optics, with the window set at 157° to the incident light beam. In excitation spectra appropriate cutoff filters were used. Great care was taken to avoid stray light.

For irradiations the light of a 1000 W Xe/Hg lamp was selected (with 12 nm bandwidth) by a Schoeffel GM152 monochromator. As a precaution appropriate cutoff filters were inserted in the beam, and the setup was otherwise kept in the dark.

Results

The electronic spectra observed after cocondensation of holmium vapors with inert gas matrices depend strongly on deposition temperature, metal evaporation rate, and photochemical treatment. In order to unravel the differences, it is necessary to describe and comment on the observations in a step-by-step fashion. Thus, we will first discuss the conditions under which only metal atoms are present, followed by the investigations of cluster formation along the three routes available: concentration studies, photomobilization, and deposition at higher temperatures.

Deposition at Slow Metal Evaporation Rate. The spectrum obtained after cocondensation with argon at an extremely slow flux of holmium (dilution Ho/Ar better than 1/10^4) at full cooling power (8−9 K) is presented in Figure 1b, with no further absorption observed in the 800−2500 nm NIR region. Already at first sight the multitude of sharp, overlapping bands centered at 400 nm matches reasonably well the gas-phase emission data[8] for holmium atoms, included as a stick spectrum in Figure 1a.

In the gas phase the holmium atom (ground state $4f^{11}6s^2$−$^4I^0_{15/2}$) exhibits a large number of transitions of small and medium intensity, dominated by five closely spaced features at 405, 410, 411, 413, and 416 nm.[8] Holmium has only one stable isotope with a nuclear spin $I = {}^7/_2$, but a large magnetic moment, which may add to the complexity of the high-resolution spectra.[28]

TABLE 1: Holmium Atom Absorptions of Site I (Photostable)[a]

gas phase			argon matrix			
nm	cm^{-1}	rI	nm	cm^{-1}	rI	diff, cm^{-1}
435.073	22 984	0.13	413.9	24 157	ovl	1173
425.443	23 505	0.13	402.9	24 817	ovl	1312
422.704	23 657	0.20	399.9	25 004	ovl	1347
417.323	23 962	0.25			nr	
416.303	24 020	0.81	394.9	25 320	0.99	1300
413.622	24 176	0.15			nr	
412.716	24 230	0.43	394.0	25 388	sh	1153
412.565	24 238	0.13			nr	
412.020	24 271	0.15			nr	
410.862	24 339	0.29			nr	
410.384	24 367	0.89	390.0	25 638	0.76	1271
406.805	24 582	0.07			nr	
405.393	24 667	0.81	386.0	25 904	0.77	1237
404.081	24 747	0.27	383.0	26 108	sh	1361
373.635	26 764	0.08			nr	
373.140	26 799	0.11			nr	
368.265	27 155	0.07			nr	
367.970	27 176	0.06			nr	
367.919	27 180	0.07			nr	
366.797	27 263	0.14	360.5	27 737	ovl	474
366.229	27 305	0.16	360.0	27 777	ovl	472
366.665	27 273	0.07			nr	
357.912	27 940	0.08			nr	
351.073	28 484	0.08			nr	

[a] rI = relative intensities; ovl = overlap, nr = not resolved.

In inert gas matrices electronic transitions of metal atoms are known[13,14,29] to be shifted, split, and broadened by the crystal field of the matrix and by the inhomogeneity of matrix sites. Furthermore, the intensity of normally forbidden transitions might be greatly enhanced due to symmetry reduction.

Under the conditions employed we can expect that only holmium atoms are present, but the complex spectrum does not allow correlation without additional information. Annealing the matrix to 25 K does produce some small spectral shifts and intensity changes, but again no unequivocal correlation.

Fortunately, selective irradiations in the 380−420 nm region allow a separation of spectral features. As an example, Figure 1c displays the result of a few minutes irradiation at 405 nm, which results in the loss of weaker features centered at 405, 415, and 445 nm. Upon prolonged irradiation at 405 nm a set of absorptions diminishes, and another set remains fairly stable. The same features are immediately lost upon irradiation at other wavelengths (e.g., 385 nm) or upon annealing to 20 K.

Although the spectrum remaining after irradiation still exhibits severe overlap, one can, by including observations from a large number of similar experiments and using the five stronger transitions for alignment, sort the initially observed features into the two sets of absorptions listed in Tables 1 and 2. Thus, we note that upon deposition holmium atoms are present in at least two different matrix sites. In both sites the argon matrix environment causes a blue shift of the atomic transitions by comparison with the gas-phase emission data, by approximately 1300 and 600 cm^{-1}, respectively. Shifts of this size are in close agreement with those observed for the d-block transition metals.[29] For example, shifts of 1300 cm^{-1} were found for yttrium atoms isolated in argon and of 500 cm^{-1} for those in krypton matrices.[29] As we noted,[5] samarium atoms in argon matrices exhibit blue shifts of up to 800 cm^{-1}.

The results are consistent with the known inhomogeneous nature of the microstructure of inert gas matrices, resulting in interstitial and/or multiple substitutional vacancies for trapping metal atoms.[30,31] Thus, site II in Table 2 (600 cm^{-1} shifts) can be associated with easily mobilized Ho atoms trapped on grain

TABLE 2: Holmium Atom Absorptions of Site II[a]

gas phase			argon matrix			
nm	cm^{-1}	rI	nm	cm^{-1}	rI	diff, cm^{-1}
435.073	22 984	0.13			nr	
425.443	23 505	0.13	416.0	23 998	0.26	493
422.704	23 657	0.20	413.9	24 157	0.60	500
417.323	23 962	0.25			nr	
416.303	24 020	0.81	402.9	24 817	0.78	797
413.622	24 176	0.15			nr	
412.716	24 230	0.43			nr	
412.565	24 238	0.13			nr	
412.020	24 271	0.15			nr	
410.862	24 339	0.29			nr	
410.384	24 367	0.89	399.9	25 004	ovl	637
406.805	24 582	0.07			nr	
405.393	24 667	0.81	394.9	25 320	ovl	653
404.081	24 747	0.27			nr	
373.635	26 764	0.08			nr	
373.140	26 799	0.11			nr	
368.265	27 155	0.07			nr	
367.970	27 176	0.06			nr	
367.919	27 180	0.07			nr	
366.797	27 263	0.14			nr	
366.229	27 305	0.16			nr	
366.665	27 273	0.07			nr	
357.912	27 940	0.08			nr	
351.073	28 484	0.08			nr	

[a] rI = relative intensities; ovl = overlap, nr = not resolved.

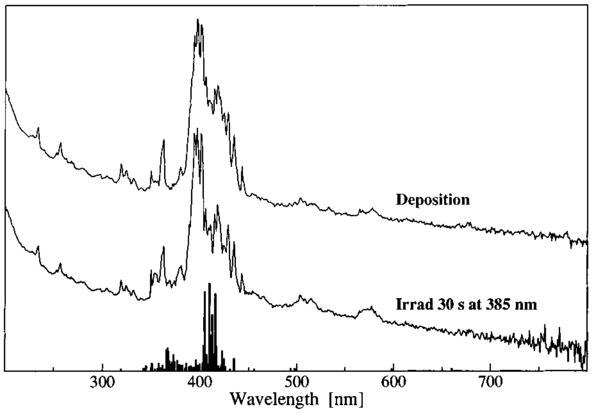

Figure 2. Comparison of the gas-phase emission spectrum of holmium atoms with the UV−vis absorption spectrum of holmium atoms isolated in krypton at high dilution (Ho/Kr < 1/10^4) and full cooling (8−9 K); and the result of 30 s narrow-band irradiation at 385 nm.

boundaries, in contrast with the association of tight bulk trapping sites to the relatively stable site I (shifts of 1300 cm^{-1}).

Figure 2 displays the result of holmium atom cocondensation with a krypton matrix, also under excellent isolation conditions. Immediately, one can notice the smaller blue shifts and the still severe splitting. However, as after several experiments not even the number of matrix sites could be established, no assignment was attempted.

Irradiation of Holmium Atoms. Close to 20 years ago the effects of "photomobilization" and "photoaggregation" of d-block metal atoms in inert gas matrices were discovered and, particularly in the case of silver, actively investigated.[32,33] This technique of creating "hot", randomly mobilized metal atoms by pumping into their resonance absorptions permits very selective formation of homonuclear and bimetallic small clusters and, as we already noted for samarium,[5] can be applied to the lanthanide series as well.

As mentioned above, narrow-band irradiation for a few minutes into resonance atomic absorptions between 380 and 405 nm, at full cooling power, results in removal of some matrix splittings and loss of intensity of some atomic bands. Already at this stage growth of weak new absorptions in the 500−600 nm region can be observed (Figure 2). Prolonged irradiations of very dilute Ho/Ar < 1/10^4 (or Ho/Kr) matrices result in simultaneous growth of two new absorptions, accompanied by a significant loss of holmium atom transition intensity. These new bands are much broader than "atomic" features; their matrix-split peaks are located at 498/504 and 558/562 nm (Figure 3). These two new doublets are tentatively assigned to the holmium dimer, Ho_2, as under the prevailing severe isolation conditions the formation of trimer and higher aggregates can be considered as negligible.

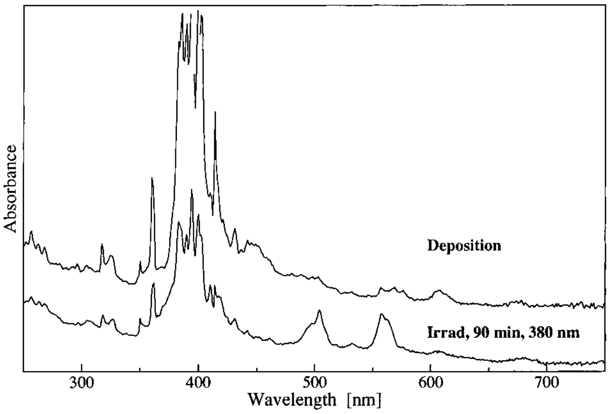

Figure 3. UV−vis spectra of holmium atoms isolated in Ar at 8−9 K, obtained after deposition and subsequent 90 min narrow-band irradiation at 380 nm, demonstrating the growth of absorptions attributed to Ho_2.

Subsequent irradiation into these dimer absorptions results in almost complete loss of these features with no other obvious changes in the spectrum: neither new features nor the "atomic bands" grow in. Interestingly, initial or subsequent "white light" irradiation results again in formation of dimer on account of atom loss, but this time the dimer site splittings are hardly noticeable, with absorptions centered at 504 and 558 nm.

Deposition at Higher Metal Evaporation Rate. In matrix isolation studies of d-block metal atom aggregation a standard route to sequential cluster formation and identification had been[33] concentration studies, in which metal deposition rates were varied by as much as 100 times, keeping all other conditions constant. This approach was taken in the holmium case, too.

Increasing the holmium sublimation rate by a factor of 2, keeping the total amount of metal deposited and all other conditions identical, results in a slight loss of intensity in the "atomic bands" and appearance of weak features in the 400−800 nm region. The effects become pronounced upon increasing the holmium sublimation rate by a factor of 10. The spectrum resulting from a deposition with 50-fold increase in metal atom rate is displayed in Figure 4, together with the base spectrum. No additional absorptions were observed in the 800−2500 nm region.

At first sight the result is disappointing. From previous experience with d-block metals[32,33] we would have expected a gradual growth of first holmium dimer and then holmium trimer features. This is not the case. As a matter of fact, the features just assigned to Ho_2 can hardly be seen in the 400−800 nm spectral region, which is dominated by more or less broad features centered at 450, 490, 515, 570, and 608 nm. Obviously, higher sublimation rate results in facile simultaneous formation of several small holmium clusters, albeit of undeterminable composition.

Some understanding can be gained from subsequent irradiations. Within seconds of irradiating into the atomic bands at

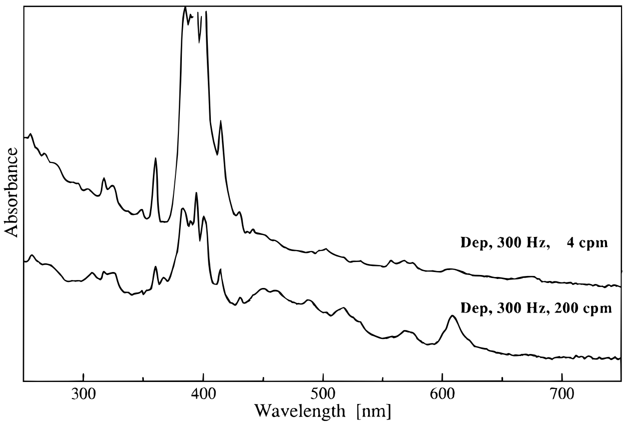

Figure 4. Comparison of the UV−vis spectra of holmium atoms isolated in argon at 8−9 K under high dilution conditions and at 50-fold higher metal evaporation rate, with all other conditions kept constant.

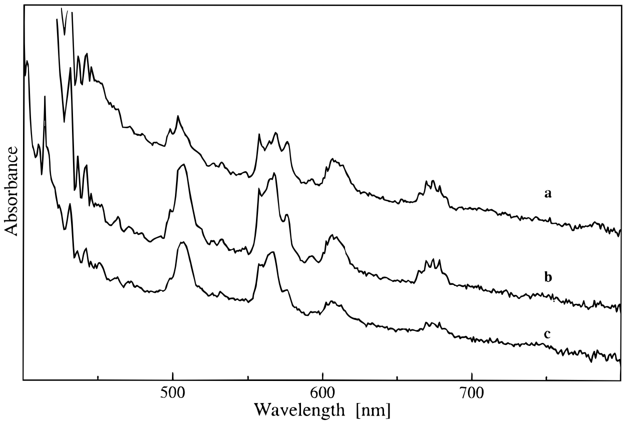

Figure 5. Comparison of the UV−vis spectrum of holmium atoms obtained (a) after cocondensation at high metal evaporation rate with argon with the results of (b) brief and (c) prolonged irradiation at 400 nm.

380 nm the 450 nm feature *vanishes*, and the two absorptions centered at 515 and 570 nm *grow in*. All the weak features in the optical spectrum are enhanced in the long-term deposition displayed in Figure 5a. At this stage a normally very weak band around 670 nm becomes intense enough to display a progression at 668/672/677/681/686 nm (average spacing 99 cm^{-1}). Furthermore, a doublet structure of the new bands becomes observable, as well as some still weak features (including two weak absorptions at 1125 and 2075 nm) for which no attempts to sort out have been made.

Annealing at this stage to more than 15 K yields gradual loss of all features, while brief irradiation results in the spectrum displayed in Figure 5b. Only the features at 515 and 570 nm grow in rapidly, while all other features, including the atomic bands, remain essentially unchanged. Subsequent prolonged irradiation (Figure 5c) brings about global loss of all absorptions with no discernible new features. Fortunately, our next series of experiments helped to solve the riddle.

Deposition at Higher Deposition Temperatures. In all experiments described above the full cooling power of the Displex closed-cycle refrigeration system was applied, resulting in temperatures of 8−9 K during and after deposition. In this way the best isolation conditions were achieved as fast as possible. A slight deliberate reduction of cooling power allows a prolonged diffusion of metal atoms and clusters before immobilization. Thus, a series of Ho/Ar cocondensation experiments were performed at temperatures between 9 and 20 K, keeping constant the conditions of slow atom sublimation previously established to yield only isolated atoms at full cooling power.

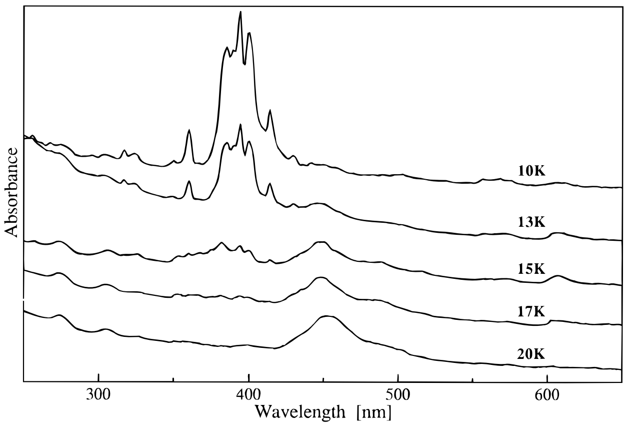

Figure 6. Effect of various deposition temperatures on the absorption spectra of Ho/Ar < 1/10^4 cocondensates (with all other conditions kept constant).

The results are presented in Figure 6. Interestingly, already at a heater-stabilized 10 K deposition temperature we note a loss of intensity in the atomic absorptions and the appearance of weak broad features in the 400−600 nm region. Annealing to 20 K for over 12 h does not change this spectrum.

Deposition at 13 K results in further loss in the atom spectrum, and growth of three weak, but distinct, features at 450, 577, and 608 nm. In the deposition at 15 K only traces of the original holmium atom absorptions are left, while now the broad 450 nm feature dominates. For depositions at 17 and 20 K this broad band is the main feature; obviously, it grows with increasing deposition temperature on account of loss of the holmium atom features. Infrared spectra in the 4000−600 cm^{-1} region confirm the absence of any impurities in the Ho/Ar matrix. Deliberate contamination of argon with water and air did not influence the 20 K cocondensation results with holmium.

It is well-known that deposition at higher temperatures leads to metal aggregation in the way of catastrophic nucleation, characterized by broad, ill-defined absorptions due to the plasmon resonance (collective electronic excitations in metal particles).[34] This effect has been studied in detail in the optical spectra of a number of metals (Na, Ag, Cu, Au), covering all stages of aggregation from atom to microcrystals.[35,36] For metal concentrations higher than 10% the sharp molecular lines abruptly disappear, and a single broad plasmon absorption, characteristic of metal microcrystals, grows in.[35,36] Thus, we initially associated the broad 450 nm feature with formation of large holmium clusters, characterized by such a plasmon resonance.

Normally, matrix isolation spectroscopy does not allow unambiguous identification of higher cluster species. However, in the holmium case we could gain additional information from photolysis studies. Irradiating into the 385−405 nm atomic transitions in order to photomobilize holmium atoms we noted, much to our surprise, that the 450 nm feature vanishes completely upon only seconds of irradiation, while the 608 nm feature remains stable. We can best present the information collected from several experiments using the data displayed in Figure 7. The upper trace exhibits the spectrum obtained after slow atom deposition at 15 K, where the intensities of the atomic transitions and the new 450 nm “plasmon” band are comparable and where the 608 nm feature is discernible. The lower trace shows the result of 20 s irradiation at 385 nm. The “plasmon” band has disappeared completely, and two new doublets grew

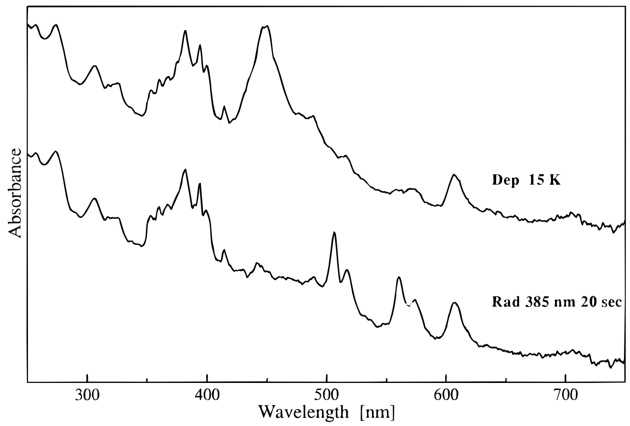

Figure 7. Comparison of the UV−vis spectra obtained after cocondensation of a slow metal flux of holmium (Ho/Ar < 1/10^4) with argon at 15 K with the result of 20 s irradiation at 385 nm.

in at 506/517 and 560/574 nm. These features immediately remind of the doublets at 498/504 and 558/562 nm, observed (Figure 3) after prolonged irradiations of dilute Ho/Ar deposits at full cooling and tentatively assigned to Ho_2. However, now the matrix splittings have increased from 5 to 12 nm, and the intensity ratios within the doublets changed.

A further clue to the identity of the broad feature we can extract from subsequent annealing. Now the "dimer" doublets diminish, and part of the "plasmon" feature reappears. Thus, taking into account the statistical chances of cluster formation and the rigidity of argon matrices below 20 K, we preliminarily assign the 608 nm feature to holmium trimer, Ho_3, and the 450 nm "plasmon" feature to holmium tetramer, Ho_4. From the information presented we can suspect that the latter exists as a weakly interacting compound of two holmium dimers. In this context we note that in Nemukhin's recent[37] calculations on the stability and structures of small holmium clusters he predicts a semitetrahedral structure as the most stable for Ho_4.

The observed temperature dependence of product yield is an important factor to take into account when cocondensing lanthanide atoms with reactive reagents to form novel complexes at temperatures above 9 K. We are therefore extending these temperature studies to other f-block members. So far we note that depositions of Gd or Sm with argon at 17−20 K yield neither atom nor cluster features, only steeply rising base lines.

Excitation and Fluorescence Spectra. In the experiments described above we could follow the stepwise, very facile light-induced mobilization and aggregation process of holmium atoms using UV−vis absorption spectroscopy. In order to gain information about the excited state species involved, we need to turn to fluorescence spectroscopy. In studies on the silver photoaggregation process some 20 years ago it was found that individual species, particular sites, and/or certain electronic transitions have "fingerprint" emission spectra.[38,39] By modifying our matrix setup, we were able to obtain absorption and fluorescence spectra from the *same* matrix. This becomes very important when considering possible photomobilization during fluorescence measurements.

When taking emission spectra for excitations of *all* atomic transitions, we note a strong emission at 580 nm, accompanied by a number of weaker emissions at 616, 624, 631, and 639 nm. However, there are subtle differences in intensity in each spectrum, which are best demonstrated in Figure 8. Spectra b, c, and d were obtained after deposition of holmium atoms in an argon matrix at 8−9 K, under conditions (Figure 8a) where only atoms are present. Figure 8b displays the emission spectrum obtained from excitation at 390 nm; Figure 8c displays the same for excitation at 414 nm. Obviously, the features around 625 nm are much stronger influenced by the presence of two matrix sites for trapped holmium atoms. Finally, Figure 8d displays the excitation spectrum recorded for the emission band at 580 nm. Comparison of the excitation with the absorption spectrum (Figure 8a) indicates that, apart from some differences in the relative peak intensities, band positions and band structure in the 350−450 nm range of the atom transitions match closely.

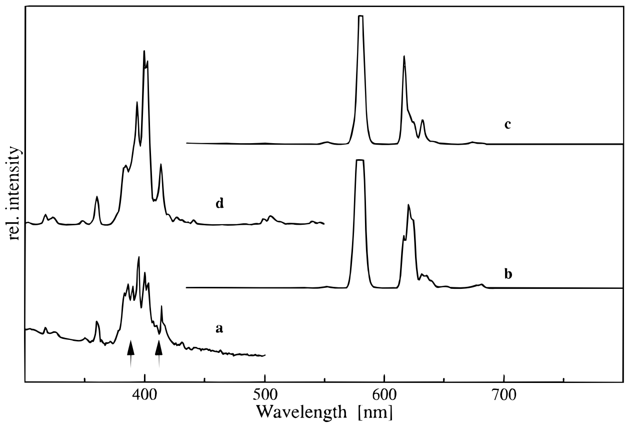

Figure 8. Superposition of (a) the absorption spectrum of holmium atoms isolated in an argon matrix, (b) the emission spectrum obtained by 390 nm excitation, (c) the emission spectrum obtained by 414 nm excitation, and (d) the excitation spectrum obtained for the emission at 580 nm.

Emissions from matrices with a higher Ho/Ar concentration exhibit a very similar spectrum when excited solely in the holmium atom region. Interestingly, excitation of the Ho_2 absorptions at 498, 503, or 557 nm again results in preferential emission at the 580 nm position, with weaker emission bands of differing intensity at 616, 624, 631, and 639 nm. To unravel the complicated interrelations, we plan a thorough separate study.

HoO in Argon. To secure our investigation, we studied the holmium oxide system as a source of possible contamination. In the past mass spectrometric work had indicated that vaporization of lanthanide(III) oxides results in formation of the corresponding monoxides and metal atom vapors in comparable amounts.[40] Binding energies, bond lengths, vibrational frequencies (for HoO $\omega_e = 784$ cm^{-1}) and dipole moments for the lanthanide monoxides from configuration interaction calculations have been compared[24] to experimental data. A single major absorption at 829 cm^{-1}, along with matrix splittings at 826 and 823 cm^{-1}, was found to be characteristic for HoO in an argon matrix[25] and was compared to the gas-phase value of 834 cm^{-1}.[22] However, the optical spectra reported for this molecule is still not unambiguous: the transitions recorded in argon matrix between 330 and 730 nm were all assigned[25] to HoO (an intense HoO absorption band was observed in the IR), but in view of the positions reported there remains the possibility that holmium atoms were present along with the monoxide. Therefore, we attempted to clarify the assignments.

Ho_2O_3 was resistively heated in a separately outgassed tantalum Knudsen cell. After careful outgassing at lower temperature the material was brought to a slow sublimation rate temperature, and the material flux was cocondensed with argon at 8−9 K. The UV−vis spectra observed are identical with those obtained for holmium atoms. Using higher deposition rates, we observe the onset of cluster formation, and the photochemical reactions are identical to those we report above for pure holmium atoms and clusters. In the infrared spectra we see, even after long depositions, no features between 1200 and 600 cm^{-1} indicative of a holmium oxide vibration, only traces of CO, CO_2, and H_2O (probably caused by a high-temperature reduction of holmium(II) oxide by carbon impurities in the Knudsen cell material).

Thus, we did a preliminary check of the codeposition of holmium atoms with neat O_2. Previously, in the case of group 8 metals, this reaction gave rise to binary transition metal dioxygen complexes of the types $M(O_2)$ and $(O_2)M(O_2)$,[41] and recently silver cation clusters were shown to form metal−oxygen complexes with dissociated oxygen.[42]

The UV−vis spectrum obtained after cocondensation of holmium with O_2 at 8−9 K exhibits neither sharp "atomic" nor broader "complex" features, but very weak shoulders at 573 and 624 nm on top of a steeply rising base line. We hope to clear up this point in a current general investigation of dioxygen reactions with lanthanide metal atoms.

Discussion

The Ho/Ar system has proven to be an interesting but difficult subject for spectroscopic investigation. It should be noted that holmium atomic spectra could only be obtained under carefully controlled conditions of excellent isolation at the lowest attainable temperature: slight variations in the deposition procedure result in absorption spectra revealing the presence of dimers and higher clusters. Even the interpretation of the absorption spectra of holmium atoms in argon matrices is made extremely difficult because of matrix shifts, line broadening, and the existence of different trapping sites characterized by blue shifts of approximately 1300 and 600 cm^{-1}, respectively.

In addition, the cluster formation process is complex, and definite assignment of absorptions to cluster species is difficult due to seemingly simultaneous growth of several different cluster species in experiments with quite different metal deposition rates. Photoactivation and photoinduced mobilization were needed to reach secure assignments, but this treatment gives cause for concern, too:

(1) The fluorescence data show two emission bands separated by some 8000 cm^{-1} from the absorption bands. Thus, there exists a very effective nonradiative energy transfer to one or more excited states. These states could be associated with the interaction of an excited state holmium atom with one or two argon atoms ("exciplex formation"). Emission from these binding states to what one might call the "ground state" of the "associated species" (which in turn would still be an excited state of the real atom ground state) would surely cause repulsion and seemingly random mobilization. In this context we note that the photomobilization of holmium atoms is at least as effective as that observed in the past for silver atoms.[38]

(2) The two main emission bands are located at 580 and 615 nm and thus overlap in part with the band positions of Ho_2 and Ho_3. Thus, secondary photoactivation has to be taken into account, which would cause formation of higher clusters if isolation conditions are not excellent.

(3) Still open remains the question of energy transfer to the quasi-stable Ho_4 species, which falls apart into holmium dimer parts upon 380 nm irradiation, that is, without direct excitation of the characteristic absorption at 450 nm! The absorption spectra give no indication of a hidden cluster feature in the 350−420 nm region, and fluorescence spectra are not possible due to the extremely sensitive photoreaction.

We are pleased to note that the results obtained are consistent with calculations on holmium dimer, trimer, and tetramer[37] done with the unrestricted Hartree−Fock (UHF) method in order to establish equilibrium geometry structures and to estimate vibrational spectra of these molecules. Although the UHF solutions were considered as not satisfactory, some tendencies in the structure of small holmium clusters have been predicted. Ho_2, Ho_3, and Ho_4 were found to be weakly bound species described by flat potential energy surfaces. Binding energy per atom slightly increases on going from dimer to tetramer and was calculated to be 6, 13, and 16 kcal/mol for Ho_2, Ho_3, and Ho_4, respectively.

Ab initio calculations for Ho_2 based on the quasirelativistic pseudopotential approach[43,44] are in good agreement[45,46] with our assignment of the transitions at 498/504 and 558/562 nm to holmium dimers. The simulations for holmium dimer were based on the $4f^n/Q = 11$ pseudopotential,[46] which best describes excitation energies in the vicinity of equilibrium by using a $5s^2 5p^6 6s^2 5d^1$ atomic configuration in the ground state. No f-electrons are considered explicitly in this approach. The computed binding energy of Ho_2 as well as transition energies and transition moments in this case is nicely consistent[45,46] with the obtained experimental data. It should be pointed out that calculations of the holmium dimer based on the $4f^{n+1}/Q = 10$ potential (for the closed-shell $5s^2 5p^6 6s^2$ electronic configuration) showed[44] practically no binding for Ho_2 system, with internuclear distance varied between 4.7 and 5.4 Å (weak van der Waals molecules).

Conclusions

UV−vis and fluorescence spectra of holmium atoms isolated in argon and krypton matrices at 9 K have been studied in the 200−800 nm region. Prolonged irradiation of dilute Ho/Ar matrices results in the simultaneous growth of two new doublets at 498/504 and 558/562 nm, attributed to the holmium dimer, Ho_2. Cocondensation of holmium atoms with argon under less stringent isolation results in the appearance of new absorptions in the 400−800 nm region, which could be attributed to the formation of Ho_3 and Ho_4. Deposition at higher temperatures indicate global clustering. Not even traces of isolated holmium atoms can be observed at deposition temperature above 17 K.

This work indicates how complex the matrix behavior of lanthanide elements might be. The data presented here for the holmium−argon system are a first step in matrix isolation studies of the intriguing cluster formation process of the f-elements.

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