Characterization of structures and spectra of holmium complexes formed in the CO and N_2 matrices

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The equilibrium geometry configurations and high-frequency IR spectra for the complexes HoL_n (L = CO, N_2, n = 1–6) are characterised by *ab initio* quantum-chemical calculations.

Matrix isolation studies provide a large body of data on the structures of *d*-metal compounds.[1,2] However, only few attempts have been performed to obtain and characterise lanthanide compounds in matrices. Direct co-condensation of metal atoms with ligands, combined with matrix isolation techniques and spectroscopic detection, offers a promising route to novel model complexes of lanthanides. Recently, experimental data on the samarium and holmium systems have been reported,[3,4] which were supported by the *ab initio* quantum-chemical simulation.[5]

In this work we present the first data on holmium complexes that can be formed in cryogenic molecular matrices of CO and N_2. Experiments with the deposition of holmium atoms in both of the matrices, controlled by UV-VIS spectroscopy, demonstrated that sharp atomic absorption bands considerably decreased after irradiation for a short time. This fact suggests that new substances were formed. These new compounds were characterised by the IR spectral bands at 1981 cm^{-1} in case of CO matrices and 2110/2097 cm^{-1} in case of N_2 matrices. This evidences that, most likely, the complexes HoL_n (L = CO, N_2) have been synthesised; however no detailed conclusions can be drawn from the experimental data.

Although it is difficult to apply quantum-chemical methods to direct calculations of the structures and spectra of lanthanide compounds,[6,7] the information gained by this modeling is of importance for the qualitative interpretation of experimental data. Since our goal is to evaluate the low-resolution vibrational spectra of conceivable complexes and to suggest molecular models consistent with the experimental observations, we report here the results of *ab initio* quantum-chemical calculations which do not pretend for high accuracy with respect to other properties. It is well known that the treatment of the transition metal carbonyl complexes in terms of quantum chemistry is very difficult.[8] However, the literature data[9] indicate that simple self-consistent field (SCF) calculations even with the small basis sets 3-21G result in reasonable predictions for the structures and high-frequency vibrational bands. A successful description of structures of lanthanide complexes at a relatively low quantum-chemical level[10] also provides support to the use of approaches that take no account of electron correlation effects and sophisticated basis sets.

The key problem in the modelling of properties of heavy elements using quantum-chemical approaches is the use of effective core potentials (or pseudopotentials) which permit one to consider explicitly only the valence shells of electrons. The main reason is the desire not only to simplify the treatment but also to present a route to incorporate relativistic effects through the parameters of the corresponding pseudopotentials. In this work we used the pseudopotential developed by Cundari and Stevens[11] for holmium, which considers the *f*-shell electrons along with (5*s*, 5*p* and 6*s*) as valence ones. Attached to this pseudopotential, the basis set [4*s*4*p*2*d*2*f*] is employed for Ho along with the conventional 3-21G basis for C, O and N. The calculations were performed using the GAMESS program package.[12] Within the selected options, the complete geometry optimization can be routinely carried out followed by the harmonic vibrational analysis for the species HoL_n (L = CO, N_2, n = 1–6).

Table 1 Calculated geometry parameters and the highest (unscaled and scaled with the factor 0.91) vibrational frequencies for the $Ho(CO)_n$ species. For n = 3, no stable minimum energy structures have been found.

Species	Symmetry	R_{HoC}/Å	R_{CO}/Å	Unscaled frequencies/ cm^{-1} (IR intensities/ D^2 $Å^{-2}$)	Scaled IR-active frequencies/ cm^{-1}
HoCO	$C_{\infty h}$	2.19	1.17	1965 (39)	1788
$Ho(CO)_2$	$D_{\infty h}$	2.35	1.14	1967 (359) 2201	1790
$Ho(CO)_4$	C_{4v}	2.47	1.14	2100 (81) 2184 2280	1911
$Ho(CO)_5$	C_{4v}	2.30 2.44	1.14 1.15	2038 (58) 2174 2188 (59) 2287	1855 1991
$Ho(CO)_6$	D_{2d}	2.41 2.47	1.15 1.13	1926 1994 (209) 2181 (109) 2190 2306	1814 1984

Table 2 Calculated geometry parameters and the highest (unscaled and scaled with the factor 0.91) vibrational frequencies for the $Ho(N_2)_n$ species. The minimum energy structure for $n = 1$ corresponds to the HoN + N composition.

Species	Symmetry	R_{HoN}/Å	R_{NN}/Å	Unscaled frequencies/ cm^{-1} (IR intensities/ D^2 $Å^{-2}$)	Scaled IR-active frequencies/ cm^{-1}
HoN···N	$C_{\infty h}$	1.91			
$Ho(N_2)_2$	$D_{\infty h}$	2.28	1.10	2117 (301) 2285	1927
$Ho(N_2)_3$	D_{3h}	2.28	1.12	2155 2967 (293)	2700
$Ho(N_2)_4$	C_{4v}	2.41	1.09	2309 (92) 2336 2445	2104
$Ho(N_2)_5$	C_{4v}	2.24 2.37	1.11 1.10	2043 (126) 2271 (186) 2354 2426	1860 2066
$Ho(N_2)_6$	D_{4h}	2.35 2.38	1.1098 1.1096	2248 (190) 2294 2297 (153) 2302 2449	2045 2090

To provide additional support to the calculation procedure, we have computed the equilibrium geometry configurations and harmonic frequencies for the well-characterised transition metal hexacarbonyls $Cr(CO)_6$ and $W(CO)_6$. The metal atoms are described by the pseudopotential parameters of Stevens *et al.*[13] (*i.e.* adjusted following exactly the same principles as for Ho) and the light atoms, by the 3-21G basis set, and the properties are evaluated within the SCF approximation. The bond lengths calculated for both of the systems [R_{CrC} = 1.999 Å, R_{CO} = 1.136 Å

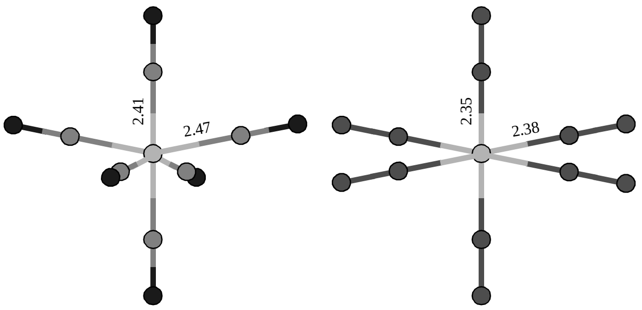

Figure 1 Geometry configurations of $Ho(CO)_6$ (left) and $Ho(N_2)_6$ (right).

for $Cr(CO)_6$ and $R_{WC} = 2.074$ Å, $R_{CO} = 1.139$ Å for $W(CO)_6$] agree, within the expected limits, with the experimental estimates[14] [$R_{CrC} = 1.914$ Å, $R_{CO} = 1.140$ Å for $Cr(CO)_6$ and $R_{WC} = 2.058$ Å, $R_{CO} = 1.141$ Å for $W(CO)_6$]. In both cases the computed highest harmonic vibrational frequencies [2305, 2219 and 2212 cm^{-1} for $Cr(CO)_6$ and 2309, 2219 and 2184 cm^{-1} for $W(CO)_6$] can be brought to a precise agreement with the experimental data confirmed by the high-level *ab initio* calculations[14,15] by using a customary scaling procedure with the scaling factor 0.91 conventional for the SCF treatment. Therefore, this particular scaling factor (0.91) is used in this work to correct the computed vibrational frequencies of HoL_n in the 2000 cm^{-1} region.

For all of the species HoL_n ($L = CO, N_2, n = 1$–6), the quartet spin multiplicity was assumed in accordance with the known ground state term of the Ho atom.[16] An additional examination of effective electronic configurations was carried out using the natural population analysis by Weinhold *et al.*[17] According to this analysis, the natural electron configuration of holmium atoms in these complexes can be described as the intermediate between the cases $\ldots 4f^{10}6s^{1}5d^{1}$ and $\ldots 4f^{10}5d^{1}$ with the formal charge at the atom between +1 and +2. A comparison of the data on the hexaligand species is most interesting. The configuration for $Ho(CO)_6$ can be described as $\ldots 4f^{10}6s^{0.45}5d^{0.8}$ with the natural charge at Ho +1.77, and for $Ho(N_2)_6$ the electronic configuration is $\ldots 4f^{10}6s^{0.25}5d^{1.16}$ with the charge at Ho +1.57.

Tables 1 and 2 show the calculation results. Note that several other stationary points (saddle points) with imaginary frequencies were detected on the potential energy surfaces. Higher energy isomers were also found [*e.g.*, the D_{3h} structure for $Ho(N_2)_5$]. Tables 1 and 2 summarise only the data on the lowest energy stable isomers.

If we compare the predicted positions of IR-active bands after the scaling (Tables 1 and 2) with those observed experimentally in the matrix studies (1981 cm^{-1} in case of CO matrices and 2110/2097 cm^{-1} in case of N_2 matrices), the majority of conceivable products $Ho(CO)_n$ and $Ho(N_2)_n$ should be rejected. Among the carbonyls, the best candidate $Ho(CO)_6$ (theoretical band at 1984 cm^{-1}) perfectly matches the experimental observations. The $Ho(CO)_5$ species with the theoretical band at 1991 cm^{-1} may also be taken into consideration. Of the dinitrogen complexes, $Ho(N_2)_6$ with the theoretical band at 2090 cm^{-1} seems to be the best candidate; however, unlike the carbonyl complexes, the $Ho(N_2)_4$ species with the band at 2101 cm^{-1} may be considered.

The predicted geometry configurations of the complexes $Ho(CO)_6$ and $Ho(N_2)_6$ are illustrated in Figure 1. According to the results of our vibrational analysis, these structures are most likely formed upon deposition of holmium atoms into the corresponding matrices. Interestingly, there is a slight distinction between the structures depending on the ligand, namely, the D_{2d} symmetry for $Ho(CO)_6$, but D_{4h} for $Ho(N_2)_6$. The above differences in the effective electronic configurations of Ho, in particular, different occupations of the 5*d* orbital (0.8 for CO and 1.16 for N_2), as well as different natural charges, may account for such a distinction. The formation of $Ho(CO)_5$ and $Ho(N_2)_4$ species cannot also be excluded.

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