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Original Investigations

Electronic structure, spectra, and thermodynamical functions of molybdenum pentachloride

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The SCF-X_α-SW method in non-relativistic and quasi-relativistic versions has been used to calculate the electronic structure, ionization potentials, energies and oscillator strengths of the optical transitions in $MoCl_5$. The electronic absorption spectrum of the gaseous $MoCl_5$ has been measured. The interpretation of the photoelectron and optical spectra of $MoCl_5$ is given. Spin-polarization effects and relativistic corrections are discussed. The thermodynamical functions of $MoCl_5$ (gas) are calculated.

Key words: Molybdenum pentachloride — Electronic structure — SCF — X_α-SW calculations — Electronic and vibrational spectra — Thermodynamical functions.

1. Introduction

Using the method of SCF-X_α-SW, we calculated earlier the electronic structure, optical spectra and some one-electron properties of $MoOCl_4$ [1], $WOCl_4$ [1, 2], $WSCl_4$ [2], MoO_2Cl_2 [3] molecules with closed electron shells. We showed that

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Offprint requests and correspondence to: V. M. Kovba it is possible on the basis of this method to reproduce correctly specific properties of experimental spectra of these molecules in the visible and UV spectrum regions and also to interpret qualitatively the observed electronic absorption spectra of related molecules ($WOBr_4$, MoO_2Br_2, WO_2Br_2).

Here the results of the calculation of the electronic structure of $MoCl_5$ by means of SCF-X_α-SW method are presented, spin polarization effects are analyzed, the role of relativistic corrections, which are the same for a $MoCl_5$ molecule as for previously investigated molybdenum oxochlorides [1, 3], is discussed, the measured electronic absorption spectrum of $MoCl_5$ in the visible and UV regions is interpreted and the thermodynamical functions of $MoCl_5$(gas) are calculated.

2. Calculation procedure

Some calculation details, such as the choice of the radii of atomic spheres, their overlapping degree, the exchange potential parameters in the intersphere and outer regions of the molecule and MO population analysis were considered in Refs. [1–3]. The $MoCl_5$ electronic structure was calculated on the basis of the X_α-SW method in the overlapping atomic spheres approximation (optimized overlapping degree was 20%) in three versions: non-relativistic spin-restricted and spin-unrestricted ones as well as a quasi-relativistic one [4, 5]. In the quasi-relativistic approximation, which is an improved Pauli approximation, relativistic corrections to the wave functions conditioned by the velocity dependence of the electron mass and by Darwin interaction were taken into account during the consistency iterations. Spin–orbital interaction was considered within the first-order perturbation theory on the basis of quasi-relativistic functions obtained in the SCF approximation. The values of spin–orbital splittings of orbital energies were also calculated with an account of interactions between energetically neighbouring MO's.

In our calculations we used the following geometrical parameters of $MoCl_5$ (C_{4v} symmetry): $R(\mathrm{Mo{-}Cl_{ax}}) = 2.348 \pm 0.032$ Å, $R(\mathrm{Mo{-}Cl_{eq}}) = 2.248 \pm 0.005$ Å, $<\mathrm{Cl_{ax}MoCl_{eq}} = 102 \pm 3°$ [6]. Earlier $MoCl_5$ was assumed [7, 8] to have a bipyramidal structure of D_{3h} symmetry.

3. Energy spectrum and MO populations

The energy spectra of occupied and vacant MO's are presented in Table 1. The calculations lead to the $MoCl_5$ ground state of the $^2B_2$ symmetry. As is seen from the table, spin polarization gives rise to a symmetric shift in opposite directions of MO systems corresponding to spin projections ↑ and ↓, with respect to the MO spectrum in the spin-restricted version. For the majority of occupied MO's the value of splitting does not exceed 0.1 eV, while for the first three unoccupied MO's – $6e^x$, $6a_1^x$, $4b_1^x$ as well as for $2b_2^x$, which is unoccupied for the MO (↓) system, it grows up to ~0.6 eV. Thus, the gap between occupied and unoccupied orbitals in the MO (↑) and MO (↓) systems differs by more than ~0.5 eV. The MO (↑) system in $MoCl_5$ is very similar to the system in $MoOCl_4$ which, as shown

Table 1. Orbital energies of occupied and unoccupied MO's of $MoCl_5$ molecule (1 spin-unrestricted, 2 spin-restricted, 3 relativistic calculation versions, 4 calculation taking into account the spin-orbital splitting). Energies are in eV

MO	1 (↑)	1 (↓)	2	3	4
$1a_1$	22.06	22.02	22.04	22.25	22.25
$1b_1$	21.75	21.70	21.73	21.89	21.89
$1e$	21.51	21.49	21.50	21.69	21.71 21.67
$2a_1$	21.45	21.53	21.47	21.67	21.67
$2b_1$	12.59	12.26	12.42	12.39	12.39
$3a_1$	12.03	11.78	11.90	11.97	11.97
$1b_2$	11.38	11.18	11.28	11.25	11.25
$2e$	11.09	10.86	10.96	10.95	10.96 10.94
$4a_1$	10.84	10.76	10.79	10.90	10.90
$3e$	10.09	10.07	10.08	10.10	10.12 10.08
$5a_1$	10.02	10.00	10.01	10.02	10.02
$4e$	9.35	9.33	9.34	9.34	9.37 9.31
$3b_1$	9.30	9.29	9.30	9.29	9.29
$5e$	9.22	9.23	9.22	9.22	9.25 9.19
$1a_2$	8.63	8.62	8.63	8.61	8.61
$2b_2$	6.83	6.15	6.48	6.37	6.38
$6e^x$	6.54	5.92	6.23	6.13	6.18 6.06
$6a_1^x$	5.23	4.70	4.96	4.90	4.90
$4b_1^x$	2.85	2.30	2.57	2.45	2.45
$7a_1^x$	1.18	1.12	1.15	1.17	1.17
$8a_1^x$	0.51	0.47	0.49	0.49	0.49
$7e^x$	0.18	0.16	0.17	0.18	0.18 0.18

below, causes similarity in spectra of these molecules in visible region. A small value of the shift of occupied MO (↑) and MO (↓) system is connected with a comparatively larger value (~2 eV) of energy difference of the MO $2b_2$↑ formed mainly by molybdenum d-AO's and lower MO's with a dominating contribution of chlorine *p*-AO's. These MO's spatially are strongly separated, and one unpaired electron on the *d*-MO weakly polarizes the system of occupied chlorine atomic shells. At the same time the lower vacant MO's formed mainly by molybdenum *d*-AO's are most strongly subjected to spin poarization. The electronic structure of $MoCl_5$ is much less affected by the relativistic corrections. For the majority of MO's the orbital energy shift due to relativistic effects does not exceed 1–2% of the MO energy in the non-relativistic approximation and makes up ~0.1 eV. The value of spin–orbital splitting for occupied MO's of the "*e*" symmetry type is equal to 0.02–0.04 eV (160–320 cm^{-1}), while for the vacant MO $6e^x$ it increases up to 0.12 eV (970 cm^{-1}). These effects are directly related to the molecular optical spectrum. The values of the relaxational shift for each optical transition in MO systems if calculated in spin-restricted and spin-unrestricted versions can be expected approximately the same, and the spectrum calculated in the spin-restricted version splits into MO (↑) and MO (↓) spectra. Comparing such a superpositional spectrum with the experimental one, one can judge how strong the spin polarization effect is. A more detailed comparison will be given to the $MoCl_5$ optical spectrum.

The analysis of populations carried out in the different versions makes it possible to single out the MO groups close in composition and to consider the polarization and relativistic effects. The MO's $1a_1$, $1b_1$, $1e$ are mainly formed by *s*-AO Cl_{eq}, and the MO $2a_1$ by *s*-AO Cl_{ax}; the MO's $2b_1$, $3a_1$, $1b_2$, $2e$, $2b_2$, $6e^x$, $6a_1^x$, $4b_1^x$ have a mixed character and are formed by chlorine *p*-AO's and molybdenum *d*-AO's, for $2b_2$ and vacant MO's the contribution of *d*-AO's being larger; the orbitals $4a_1$, $3e$, $4e$, $5e$ are of a mixed type with different contributions of *p*-AO Cl_{ax} and *p*-AO Cl_{eq}; the MO's $5a_1$, $3b_1$, $1a_2$ are formed completely or mainly by chlorine *p*-AO's (Table 2). Thus, $2b_2-6e^x$ transition must correspond to $d-d$ transition, and the other ones on the MO's $6e^x$, $6a_1^x$, $4b_1^x$ must correspond to charge transfer (from a ligand to a metal) transitions. The spin polarization and relativistic effects do not affect general conclusions concerning the MO composition.

Table 2. The MO populations (%) in $MoCl_5$ (spin-restricted calculation)

	Cl_{ax}		Cl_{eq}		Mo			
MO	*s*	*p*	*s*	*p*	*s*	*p*	*d*	*f*
$1a_1$	0.80	—	92.96	0.87	3.55	0.16	1.46	0.19
$1b_1$	—	—	93.17	0.61	—	—	6.00	0.22
$1e$	—	—	96.15	0.15	—	2.47	0.57	0.65
$2a_1$	95.99	0.13	0.81	—	0.30	0.88	1.67	0.22
$2b_1$	—	—	2.33	62.14	—	—	35.32	0.21
$3a_1$	0.11	5.96	2.00	63.42	4.67	0.51	23.30	0.03
$1b_2$	—	—	—	76.37	—	—	23.52	0.11
$2e$	—	7.74	0.36	63.56	—	2.23	25.83	0.28
$4a_1$	0.63	65.35	0.27	14.62	7.95	0.69	9.65	0.84
$3e$	—	24.49	0.20	68.10	—	5.66	1.07	0.48
$5a_1$	0.06	4.70	0.01	91.73	—	3.02	0.26	0.23
$4e$	—	13.71	0.09	82.19	—	0.89	0.80	2.31
$3b_1$	—	—	0.01	98.82	—	—	0.02	1.14
$5e$	—	45.29	0.03	53.23	—	0.16	0.48	0.81
$1a_2$	—	—	—	100	—	—	—	—
$2b_2$	—	—	—	27.71	—	—	72.18	0.11
$6e^x$	—	5.41	0.39	21.57	—	2.27	69.93	0.43
$6a_1^x$	3.63	17.38	0.34	10.93	2.71	5.83	58.35	0.83
$4b_1^x$	—	—	13.73	28.62	—	—	55.94	1.71
$7a_1^x$	19.65	0.03	74.67	0.41	2.22	0.02	1.18	1.82
$8a_1^x$	89.43	—	1.02	6.56	0.02	2.21	0.35	0.41
$7e^x$	—	6.84	88.83	3.46	—	0.75	—	0.12

Table 3. Atomic effective charges and one-electron properties of $MoCl_5$. μ is a total dipole moment, θ_{xx}, θ_{yy}, θ_{zz} are components of the quadrupole moment tensor, χ_{mean}, χ_{xx}, χ_{yy}, χ_{zz} are a mean value and components of the diamagnetic susceptibility. All the values are calculated in the centre-of-mass coordinate system

	Spin-restricted calculation	Spin-unrestricted calculation
^{q}Mo	+0.91	+0.92
$^{q}Cl_{ax}$	−0.12	−0.10
$^{q}Cl_{eq}$	−0.20	−0.20
$\mu(D)$	4.5125	
$\theta_{xx}, \theta_{yy}(B)$	−9.83	
$\theta_{zz}(B)$	+19.66	
χ_{mean}(ppm)	−1377.10	
χ_{xx}, χ_{yy} (ppm)	−1292.84	
χ_{zz} (ppm)	−1545.60	

The calculated values of spin–orbital splitting of core levels constitutes: Mo $2p-107.37$ eV, $3p-17.73$ eV, $3d-3.36$ eV, $4p-2.56$ eV, Cl $2p-1.71$ eV. These are close to the spin–orbital core level splitting values in free Mo and Cl atoms [9].

Table 3 presents some one-electron properties of the $MoCl_5$ molecule: effective atomic charges, the dipole moment value, the quadrupole moment tensor components and diamagnetic susceptibility. In the transition state approximation electron affinity of the $MoCl_5$ molecule was calculated equal to 3.53 eV.

4. Photoelectron spectrum

The photoelectron spectrum (PES) of $MoCl_5$ was measured in Ref. [10] and interpreted by analogy with the PES of niobium and tantalum pentahalides. All the molecules were assumed to have bipyramidal structure (D_{3h}). On the ground of the transition state approximation and spin-restricted version we calculated $MoCl_5$ (C_{4v}) ionization potentials (IP) as well as IP for the highest occupied MO's in the spin-unrestricted and relativistic versions. The values of the calculated IP are in Table 4. Corrections due to polarization and relativistic effects are seen to be the most significant for the $2b_2$ MO. For the other MO's the IP spectrum practically coincides with the results of spin-restricted calculations. The MO's which should be observed in PES can be divided into five groups: $2b_2$; $1a_2$, $5e$, $3b_1$, $4e$; $5a_1$, $3e$; $4a_1$, $2e$, $1b_2$; $3a_1$, $2b_1$. Corresponding values of the calculated IP lie in the intervals: ~9.3 eV, 11.2–12.0 eV, 12.5–12.6 eV, 13.6–13.8 eV, 14.6–15.2 eV which are close to the experimental values of the band maxima in the PES of $MoCl_5$–9.27 eV, 10.73 eV (shoulder), 11.27 eV, 11.96 eV, 12.86 eV, 13.95 eV, 14.52 eV (shoulder). So, except for the first peak, all the bands observed in PES are connected with ionization of several MO's including degenerate orbitals of "e" symmetry with the spin–orbital splitting value equal to 0.04–

Table 4. Ionization potentials and PES bands for $MoCl_5$. IP in eV

MO	Spin-restricted calculation	Spin-unrestricted calculation	Relativistic calculation	Experimental data [10]
$1a_1$	24.74			
$1b_1$	24.46			
$1e$	24.21			
$2a_2$	24.50			
$2b_1$	15.16			
$3a_1$	14.57			14.52
$1b_2$	13.82			
$2e$	13.57			13.95
$4a_1$	13.67			
$3e$	12.60			
$5a_1$	12.52			12.86
$4e$	11.91		11.91	
$3b_1$	11.89		11.88	11.96
$5e$	11.78	11.71	11.78	
$1a_2$	11.24	11.17	11.24	11.27
				10.73
$2b_2$	9.39	9.67	9.29	9.27

0.06 eV. For a more unambiguous assignment one should estimate quantitatively the ionization cross-section of corresponding MO's.

5. Optical spectrum

The spectrum of gaseous $MoCl_5$ was originally studied by Bader et al. [11]. However, their sample of $MoCl_5$ evidently contained some amount of $MoOCl_4$. Such a conclusion is based on two reasons. First, in the IR region of the spectrum a band 1006 cm^{-1} was observed, which the authors assigned to the transition between the components of the ground electronic state. As shown by the subsequent investigations of the vibrational spectrum of $MoOCl_4$ [12, 13], this band belongs however to molybdenum oxotetrachloride and is connected with molybdenum–oxygen stretching vibration. Second, as temperature was going up a rapidly increasing chlorine absorption band was observed on the edge of the UV region [11]. $MoOCl_4$ is heat-unstable, and when heated, it decomposes producing chlorine [14]. It was rather this process than decomposition of $MoCl_5$ into $MoCl_4$ and chlorine, which proceeds at higher temperatures than those of the spectrum measurements [15, 16].

The molybdenum pentachloride vapour absorption spectrum shown in Fig. 1 was measured on a spectrophotometer SF-20. The $MoCl_5$ sample was kindly supplied by V. N. Zavadovskaya.

The optical transition energies for the $MoCl_5$ molecule were calculated in a framework of the spin-restricted and spin-unrestricted X_α-SW techniques and the transition state approximation. Oscillator strengths for one-electron transitions were calculated with a potential gradient as the dipole moment operator.

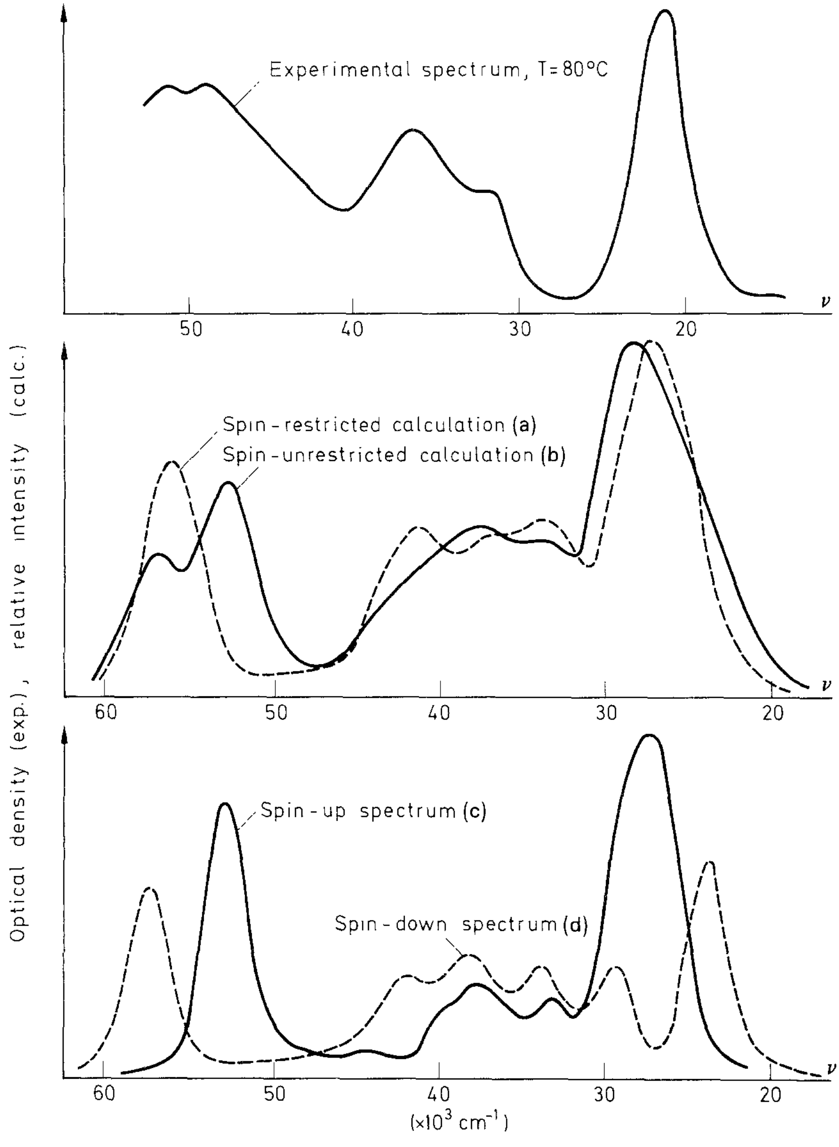

Fig. 1. Experimental and theoretical spectra of $MoCl_5$ molecule in UV and visible regions

Transition energies and oscillator strengths are presented in Table 5. Besides, for the most low-lying transitions relativistic effects were taken into account. The relativistic corrections to the transition energy values in the spin-restricted version turned out not to exceed 0.10–0.15 eV. The theoretical spectra are presented in Fig. 1. The theoretical spectrum 2 "a" was obtained within the spin-restricted approach. The spectrum "b" is a superposition of spectra of MO (↑) and MO (↓) systems. The Figure also shows the separate spectra of MO (↑) and MO (↓) systems ("c", "d"). The theoretical spectra were obtained as a superposition of

Table 5. Transition energies (ΔE in eV) and oscillator strengths (f) in $MoCl_5$

	Spin-rest. cal. culation		Spin-unrest. calculation				Relativistic calculation
Transition	ΔE	f	ΔE ($\downarrow$)	f	ΔE ($\uparrow$)	f	ΔE
$2b_2$–$6e^x$	0.26				0.29		0.24
$1a_2$–$6e^x$	2.85	0.042	2.95	0.020	2.31	0.034	
$5e$–$2b_2^x$	3.17	1.674	3.31	1.520	—	—	3.32
$4e$–$2b_2^x$	3.31	0.204	3.42	0.242	—	—	3.45
$5e$–$6e^x$	3.36	0.200	3.56	0.063	2.92	0.226	
$4e$–$6e^x$	3.49	0.730	3.63	0.613	3.01	0.498	3.61
$3b_1$–$6e^x$	3.51	0.939	3.61	0.433	2.98	0.736	3.62
$3e$–$2b_2^x$	4.00	0.188	4.12	0.172	—	—	
$5a_1$–$6e^x$	4.16	0.002	4.29	0.002	3.67	0.004	
$3e$–$6e^x$	4.18	0.612	4.34	0.274	3.70	0.462	
$5e$–$6a_1^x$	4.54	0.360	4.71	0.143	4.16	0.239	4.59
$2e$–$2b_2^x$	4.68	0.150	4.82	0.135	—	—	
$4e$–$6a_1^x$	4.78	0.026	4.84	0.027	4.35	0.020	
$2e$–$6e^x$	4.91	0.165	5.04	0.084	4.61	0.073	
$1b_2$–$2b_2^x$	5.06	0.003	5.21	0.002	—	—	
$4a_1$–$6e^x$	5.16	0.268	5.23	0.144	4.66	0.167	
$1b_2$–$6e^x$	5.28	0.092	5.41	0.042	4.94	0.058	
$3e$–$6a_1^x$	5.38	0.001	5.49	0.001	4.99	0.001	
$5a_1$–$6a_1^x$	5.40	0.130	5.51	0.062	5.01	0.073	
$3a_1$–$6e^x$	5.85	0.040	5.96	0.017	5.54	0.044	
$2e$–$6a_1^x$	6.19	0.012	6.27	0.007	5.95	0.008	
$4a_1$–$6a_1^x$	6.21	0.001	6.31	0.001	5.81	0.001	
$2b_1$–$6e^x$	6.33	0.015	6.42	0.005	6.10	0.014	
$5e$–$4b_1^x$	6.96	0.125	7.23	0.011	6.53	0.151	
$3b_1$–$4b_1^x$	7.05	0.242	7.17	0.118	6.63	0.134	
$4e$–$4b_1^x$	7.12	0.030			6.65	0.133	

Gaussians with a width 0.4 eV, which describe intensity distribution for each optical transition. The maximum value of each Gaussian corresponds to the oscillator strength calculated with an account of energy dependence of the total transition intensity proportional to $(\Delta E)^2$, where ΔE is transition energy.

Comparison of the experimental and calculated spectra shows that on the whole the theoretical spectrum reflects correctly the structure of the experimental spectrum, a better agreement being reached in the spin-unrestricted version. All completely occupied MO's, that determine the initial state of one-electron transitions, are practically degenerate in what concerns the value of spin splitting. Thus, in spin-up and spin-down systems it is only spin splitting of vacant MO's that can be observed in the spectrum.

Likeness of the populations of the upper occupied MO's (except for $2b_2$) of $MoOCl_4$ and $MoCl_5$ molecules as well as similarity in the energy spectrum shift of the upper occupied and lower vacant MO's in transition from one molecule to another make on the whole the absorption spectra of these molecules rather similar in visible and UV regions. The appearance of some additional structures in the spectrum of $MoCl_5$ is connected, as has already been said, with the spin polarization of $MoCl_5$ vacant MO's.

The structure of the optical spectrum of $MoCl_5$ was analyzed in terms of one-electron transitions taking into account spin polarization. These effects are model representations [17] of more complicated multiplet splitting effects resulted from the spin decoupling in the initial and final states. Nevertheless as is seen from our calculations, such model representations are very effective means of analyzing complicated electron spectra of heavy molecules when each of the observed bands of the experimental spectrum is in fact a superposition of a large number of electronic transitions.

6. Thermodynamical functions

The thermodynamical functions of the gaseous $MoCl_5$ were already calculated twice [18, 19]. In both cases the molecular structure D_{3h} was assumed according to the available results of electron-diffraction studies [7, 8], and the multiplicity of the electronic ground state was taken equal to two. The vibrational frequencies of a molecule were either completely [18] or partially [19] estimated. The energies (E) and statistical weights (g) of excited electronic states were evaluated only in ref. [18] ($E = 7000\ \mathrm{cm}^{-1}$, $g = 2$ and $E = 14\,000\ \mathrm{cm}^{-1}$, $g = 2$).

A good agreement between the experimental and calculated electron spectra of $MoCl_5$ in the visible and UV regions gives ground for constructing a system of excited electron states of a molecule and for calculating consequently the thermodynamical functions of $MoCl_5$ (gas). In the framework of one-electron X_α-SW

Table 6. Electronic state symmetry types corresponding to the one-electron excitations

Transition type	Unpaired electron configuration	State type
a_1–a_1	$a_1^1 b_2^1 a_1^1$	$^2B_2$ ($^4B_2$)
e–a_1	$e^3 b_2^1 a_1^1$	^2E (^4E)
b_1–b_1	$b_1^1 b_2^1 b_1^1$	$^2B_2$ ($^4B_2$)
e–b_1	$e^3 b_2^1 b_1^1$	^2E (^4E)
b_2–b_2	$b_2^1 b_2^2$	$^2A_1$
e–b_2	$e^3 b_2^2$	^2E
a_1–e	$a_1^1 b_2^1 e^1$	^2E (^4E)
b_1–e	$b_1^1 b_2^1 e^1$	^2E (^4E)
a_2–e	$a_2^1 b_2^1 e^1$	^2E (^4E)
b_2–e	$b_2^1 b_2^1 e^1$ or $b_2^0 e^1$	^2E (^4E) or only ^2E
e–e	$e^3 b_2^1 e^1$	$^2A_1$, $^2A_2$, $^2B_1$, $^2B_2$ ($^4A_1$, $^4A_2$, $^4B_1$, $^4B_2$)

approximation, many of the excited states cannot, be exactly resolved in symmetry and multiplicity. To calculate the thermodynamical functions, it is however sufficient to use averaged energies of such groups of excited states. Table 6 presents types of excited states for different transitions. We took into account excited electron states with energies ≲5–6 eV obtained within the spin-restricted version. Excited states with similar energies were united and taken with a summary statistical weight. The energies of excited states (in cm^{-1}) and the statistical weights used in the calculation of thermodynamical functions were as follows: 2100 (4), 23 000 (12), 26 000 (8), 28 000 (60), 34 000 (40), 39 000 (52), 43 000 (44). The errors were taken to be 10%.

According to the C_{4v} structure of the $MoCl_5$ molecule, the bands in IR and Raman spectra were reassigned. In the Raman spectrum of gaseous $MoCl_5$ the bands of 418, 390, 313, 200, 175 and 100 cm^{-1} were observed [20], and in the IR spectrum the bands of 425, 320, 150 and 100 cm^{-1} [21]. The bands were reassigned by analogy with vibrational frequencies of the $MoOCl_4$ molecule (Table 7) which also has C_{4v} symmetry and contains the $MoCl_4$ fragment with similar structure parameters ($R(Mo—Cl) = 2.278$ Å, $\angle OMoCl = 103°$ [22]). As is seen from Table 7, the values of the vibrational frequencies, which are for the most part due to the $MoCl_4$ fragment, are close or coincide in both the molecules. The values of the frequencies ν_1 and ν_8 with the participation of Cl_{ax} must be much lower than ν_1 and ν_8 in $MoOCl_4$ which are oxygen atom vibrations. The vibration ν_5 is active only in the Raman spectrum and therefore the band 100 cm^{-1} observed in the IR spectrum of $MoCl_5$ should evidently be assigned to bending

Table 7. Vibrational frequencies (in cm^{-1}) of $MoCl_5$ and $MoOCl_4$ molecules

Vibration ($X' = Cl, O$)	$MoCl_5$ ($Cl'MoCl_4$)	$MoOCl_4$ [21] ($OMoCl_4$)
$\nu_1(A_1)$ stretch. Mo-X	313 [20]	1015
$\nu_2(A_1)$ stretch. $MoCl_4$	390 [20]	392
$\nu_3(A_1)$ bending $MoCl_4$	175 [20]	175
$\nu_4(B_1)$ stretch. $MoCl_4$	(310)	310
$\nu_5(B_1)$ bending $MoCl_4$	100 [20]	105
$\nu_6(B_2)$ bending $MoCl_4$	200 [20]	212
$\nu_7(E)$ stretch. $MoCl_4$	418 [20]	400
$\nu_8(E)$ bending XMoCl	100 [21]	253
$\nu_9(E)$ bending $MoCl_4$	150 [21]	150

vibration ν_8. Both the vibrations, although different in symmetry, are connected with the change of angles $\angle Cl_{ax}MoCl_{eq}$, and the coincidence of their frequencies within the experimental error is quite probable. The errors in accepted values of the vibrational frequencies are 2–3 cm^{-1}, except the error in the estimated frequency ν_4 which is taken equal to 20 cm^{-1}.

The thermodynamical functions of $MoCl_5$ (gas) are calculated in the "rigid rotator – harmonic oscillator" approximation. Summary errors in the values of $-(G_T^0 - H_0^0)/T$ at 298.15, 500, 1000, 3000, 6000 K, calculated according to Ref. [23], make up 3.0, 5.0, 8.0, 1.0, 16.0 J deg^{-1} mol^{-1}. The values of the thermodynamical functions are represented in the Table 8.

Table 8 also presents the contributions to the thermodynamical functions connected only with excited electronic states of a molecule. As seen, for $MoCl_5$ it is only the first low-lying excited electronic state that is essential. The contributions of the other states with energies ≥2.5–3 eV are negligibly small. The Table shows that the largest differences (4–5% of the absolute value at 1000 K and ~8% at 6000 K) are observed in the case of C_p^0, the dependence $C_p^0(T)$ has a wavelike character, i.e. it increases, reaches some maximum (~1500 K), then passes through the minimum (~3500 K) and then increases again. If the excited electronic states are disregarded, C_p^0 simply increases with the temperature. Changes in the values of $H_T^0 - H_0^0$ are less significant (~1–3%), and for $-(G_T^0 - H_0^0)/T$ and S_T^0 the corrections do not exceed 1% even at high temperatures.

The contribution of excited electronic states to the values of the thermodynamical functions of $MoCl_5$ is on the whole insignificant because all the states,except the first, have a high excitation energy, and a first excited state has a comparatively small statistical weight. On the other hand for the other molybdenum halides, for example, $MoCl_4$, one can expect the presence of several relatively low-lying electronic states, which should give a larger contribution than in the case of $MoCl_5$.

Table 8. Thermodynamical functions of $MoCl_5$ (gas)

	C_p^0	x	$-(G_T^0 - H_0^0)/T$	x	S_T^0	x	$H_T^0 - H_0^0$	x
T K	J $degree^{-1}$ mol^{-1}						kJ mol^{-1}	
298.15	121.285	0.068	319.653	0.001	408.992	0.008	26.636	0.002
500	129.874	1.428	369.834	0.039	474.064	0.277	52.115	0.119
1000	137.982	6.142	447.677	0.773	567.249	3.004	119.572	2.231
2000	136.763	4.033	534.160	3.041	662.893	6.887	257.467	7.695
3000	135.055	2.158	586.888	4.561	717.965	8.104	393.233	10.631
4000	135.257	2.302	624.742	5.523	756.792	8.690	528.200	12.667
5000	138.247	5.265	654.298	6.225	787.235	9.461	664.685	16.182
6000	144.291	11.294	678.646	6.874	812.935	10.914	805.734	24.241

x = contributions related to excited electronic states of $MoCl_5$ molecule.

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