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Publication Date

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Submitted to Journal of Chemical Physics

LBL-8457 c.2
Preprint

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December 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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THE ELECTRONIC STRUCTURE OF UCl_6: PHOTOELECTRON SPECTRA AND SCATTERED WAVE Xα CALCULATIONS*

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November 1978

ABSTRACT

Helium-(I) and -(II) excited photoelectron (p.e.) spectra of UCl_6 are reported. Experimental ionization energies agree well with those predicted by a pseudo-relativistic scattered wave Xα calculation; further support for the proposed assignments is provided by a consideration of intensity patterns in the spectra. Attention is ultimately focused on the relationship between ionization energies and charge transfer electronic excitation energies in hexahalo complexes. Further experimental work is required to establish an assignment for the electronic absorption spectrum of UCl_6.

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*This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.
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Introduction

Octahedral systems are of central importance in the general field of coordination chemistry, the electronic structure of hexahalo transition metal and actinide complexes having aroused widespread interest. In particular there have been several attempts to interpret charge transfer spectra of hexahalides in relation to the orbital energy sequence for electronic subshells of dominantly halogen character.[1] Photoelectron spectroscopy (PES) provides direct insight into the ordering of electronic levels within the ligand manifold. Nonetheless few metal hexahalides have been studied by gas phase PES, attention so far being restricted to the fluorides of molybdenum, tungsten[2] and uranium.[2,3] In the present communication we report He(I) and He(II) PE spectra of UCl_6 and compare the results of our experiments with relativistic scattered wave Xα calculations.

Experimental

UCl_6 was prepared by the passage of Cl_2 over resublimed UCl_4 at 350°C.[4] The crude compound was purified by vacuum sublimation at 110°C (10^{-3} Torr) to yield dark black-green crystals. It is claimed that the compound prepared by this method contains traces of UCl_5.[5] However, a sample of brown UCl_5 obtained as a byproduct of the reaction between UO_2 and CCl_4 at 450°C yielded PE spectra essentially identical to those of UCl_6. It appears then that any UCl_5 present in our sample disproportionates to yield UCl_6 and involatile UCl_4

under the dynamic vacuum conditions pertaining to the spectrometer. We note in passing that neither He(I) nor He(II) PE spectra contained signals attributable to ionization of f electrons. This provides further evidence that negligible concentrations of the f^1 species UCl_5 are present in the vapor phase.

PE spectra were measured on a Perkin Elmer PS16/18 spectrometer modified for He(II) measurements by the inclusion of a hollow cathode discharge lamp and high current power supply. Usable count rates were obtained in the temperature range 90°C-120°C. Spectra were calibrated by reference to signals due to admixed inert gases and nitrogen. Band areas were estimated from raw spectra with the aid of a Dupont 310 curve resolver and were corrected to allow for variation in analyzer transmission function with electron kinetic energy.[6]

He(I) and He(II) PE spectra are shown in Fig. 1, whilst ionization energies and relative band areas are collected in Table I.

Computational Details

The computational approach adopted in the present work follows the lines described by Slater.[7] However, the uranium core electron charge density was derived from a relativistic calculation and a quasi-relativistic version of the scattered wave method was used in the molecular calculation.[8] This routine does not include spin-orbit coupling.

The U-Cl distance was taken as 0.242nm, being a value obtained from an x-ray diffraction study on the solid.[9] The muffin-tin radii were chosen as follows: the uranium sphere size (r_U = 0.1475nm) was determined by consideration of calculations on UF_6,[10a] the value adopted being that which yielded closest correspondence with discrete variational Xα calculations on this molecule;[10b] the chlorine radius (r_{Cl} = 0.1092nm) was also chosen by reference to calculations on UF_6 and was such that chlorine spheres touched an imaginary sphere of radius 0.1328nm; the outer sphere was chosen to touch the chlorine spheres (r_{OS} = 0.3512nm). Atomic exchange scaling parameters were those calculated by Schwarz[11,12]; $\alpha_U = 0.692$, $\alpha_{Cl} = 0.7233$. Extramolecular and intersphere scaling parameters were obtained by averaging the atomic parameters (α = 0.7188). Core electron densities for uranium ([Xe]$4f^{14}$) and chlorine ([Ne]) were "frozen" at their atomic value; other electron distributions were allowed to vary in the SCF calculations. The results for the ground state molecules are shown in Fig. 2 as are the orbital energies calculated for U and Cl free atoms.

Ionization energies of UCl_6 were calculated by the transition state method of Slater[7] and are given in Table II. This table also contains normalized charge distributions within each sphere for the various electronic levels.

Discussion

The bands apparent in the PE spectra of UCl_6 correspond to the set of seven electronic subshells of dominant chlorine 3p atomic character. As with other metal chlorides,[13-15] we fail to observe bands attributable to ionization of chlorine 3s electrons in the He(II) spectra. Uranium 6p ionizations are also absent from our spectra.

There is remarkably good agreement between calculated and experimental ionization energies, it being particularly encouraging to find that the overall spread of ionization energies predicted (1.86 eV) is close to that found in the PE spectra (2.00 eV). The most straightforward interpretation of our data is therefore based on the assumption that the theoretical sequence of ionization energies is preserved in the experimental spectra. The root mean square deviation between calculated and empirical ionization energies is then as small as 0.29 eV. However, where PE bands are very closely spaced there is clearly some room for debate as to the ordering of levels and especially in the regions of bands c and d the assignment should be regarded as tentative.

Intensity patterns in the PE spectra lend support to our overall assignment. In particular, we note that if intensities are normalized relative to the first band (a), then at He(II) excitation each of the other band systems (b-e) undergoes an increase in relative intensity. Moreover, if one makes the reasonable assumption that band a relates to a triply degenerate subshell, then it is found that in the He(II) spectra intensities are uniformly higher than expected on purely statistical grounds. Similar behavior is found in spectra of the group IVA halides[13] where the leading PE band is associated with the purely chlorine based non-bonding t_1 molecular subshell. In octahedral actinide systems only the t_{1g} subshell is of pure chlorine 3p atomic character, this being consistent with the assignment of band a to this particular level.

The He(II) intensity patterns are largely a consequence of the very low cross-section for chlorine 3p atomic orbitals. The atomic cross-section profile for the valence p shell of chlorine calculated using the RPAE method[16] is similar to that found experimentally for argon[17] and contains a broad Cooper minimum centered around $h\nu = 40$ eV. Application of the Gelius model to the He(II) PE spectrum of $HgCl_2$ leads to a rough estimate of 0.2Mb for the chlorine 3p one-electron cross-section,[6,18] a value in agreement with the RPAE calculation. Metal based atomic orbitals typically have higher cross-sections. In particular we estimate that the one-electron cross-section for the 5f orbital of uranium is of the order 1.4Mb. This value is based on an analysis of PE spectra of metal tetrahydroborates.[18,19] Intensity patterns in the He(II) PE spectrum of $U(C_8H_8)_2$ [20] suggest that the uranium 6d cross-section is somewhat lower than this, but presumably still higher than 0.2Mb.

It follows that the intensity in He(II) spectra of bands associated with nominally chlorine based levels may be enhanced by covalent mixing with metal d or f orbitals.[6] In this connection it is noteworthy that the overlapping bands *c* and *d* are relatively stronger than the broad band *e* in He(II) spectra. This observation is in tune with the idea that band *e* relates to molecular subshells with 6d character and bands *c* and *d* to levels which can assume metal 5f character. To summarize, then, the intensity patterns in the spectra appear consistent both with the proposed sequence of orbital energies and with another feature of the calculations, namely that both 6d and 5f covalency is of importance in the bonding in UCl_6.

It is of some interest to consider our spectral assignment in relationship to electronic absorption spectra of hexahalo complexes. Detailed studies of transition metal hexachloro complexes such as $IrCl_6^{2-}$ indicate that the first charge transfer band is associated with the electric dipole parity forbidden excitations $t_{1g}(\pi) \rightarrow t_{2g}(d)$. The parity allowed transitions $t_{1u}(\sigma+\pi) \rightarrow t_{2g}(d)$ occur at higher energy and give a large negative C term in the solution phase MCD spectrum.[21] These observations clearly suggest an occupied orbital sequence $t_{1g} > t_{1u}$, consistent with that proposed for UCl_6. In UF_6 the first absorption band[22-24] apparently corresponds again to a parity-forbidden process ($\varepsilon_{max} = 54 cm^2 \cdot mol^{-1}$, $\lambda_{max} = 369 nm$) even though the lowest unoccupied levels are undoubtedly of dominantly uranium 5f character and therefore of odd parity. Although it has been variously suggested that the first electronic absorption band for UF_6 is associated with $t_{1g} \rightarrow \gamma_u(5f)$[25,26]

or $a_{1g} \rightarrow \gamma_u(5f)$[25] excitations, the discrete variational $X\alpha$ calculations of Ellis and co-workers[10] favor instead assignment to $t_{1u} \rightarrow \gamma_u(5f)$ processes. It appears moreover that the first band in the PE spectrum of this molecule is associated with the t_{1u} ligand subshell; uranium 6p - fluorine 2p $\sigma - \sigma$ overlap apparently plays a major role in destabilizing the t_{1u} orbitals. This effect is expected to be less important in UCl_6 (because of the greater difference in energy between U(6p) and Cl(3p) AOs) and indeed our calculations and PE spectra indicate that the first ionization process is associated with the t_{1g} subshell.

Somewhat surprisingly then the electronic absorption spectrum of vapor phase UCl_6[22] shows a qualitative resemblance to that of UF_6, a relatively weak absorption band ($\lambda_{max} \approx 498$nm) preceeding the onset of strong continuous absorption at shorter wavelengths ($\lambda < 415$nm). Of course it must always be borne in mind that the sequence of optical excitation energies may differ from the sequence of orbital ionization energies because of differences in electron-electron repulsion energies. Ignoring differential relaxation effects and correlation energy changes the difference in ionization energy (Δ_1) for t_{1g} and t_{1u} orbitals is quite simply the negative of the difference in orbital energies.

$$\Delta_1 = I(t_{1g}) - I(t_{1u}) = -(\varepsilon(t_{1g}) - \varepsilon(t_{1u}))$$

By contrast electronic excitation energies depend not only on orbital energy differences between occupied (o) and virtual (v) levels, but also upon the electron-electron repulsion energy, R_{ov}, between the two levels involved. It follows that the difference in electronic excitation energy for transitions to a level $\gamma_u(5f)$ originating in t_{1g} and t_{1u} orbitals respectively is given by Δ_2 where:

$$\begin{aligned}\Delta_2 &= E(t_{1g} \rightarrow \gamma_u(5f)) - E(t_{1u} \rightarrow \gamma_u(5f)) \\ &= -(\varepsilon_{t_{1g}} - \varepsilon_{t_{1u}}) - (R_{t_{1g}\gamma_{u(5f)}} - R_{t_{1u}\gamma_{u(5f)}}) \\ &= \Delta_1 - (R_{t_{1g}\gamma_{u(5f)}} - R_{t_{1u}\gamma_{u(5f)}})\end{aligned}$$

Transition state calculations of electronic excitation energies (Table III) reveal that in general $\Delta_2 < \Delta_1$,[27] but that for each of the f-shells (t_{1u}, t_{2u}, a_{2u}) $\Delta_2 > 0$, i.e., the sequence of ionization and excitation energies are the same. Thus our calculations do <u>not</u> lend support to the view that the assignments of the electronic absorption spectra of UF_6 and UCl_6 are similar. However, we feel it would be dangerous at this stage to hazard an assignment for the spectrum of UCl_6 since values for extinction coefficients are not quoted in reference 22. Furthermore, marked differences between the vapor phase spectrum and that obtained from a solution of UCl_6 in C_7F_{16} require explanation. It is to be hoped that these matters will be the subject of future investigations.

ACKNOWLEDGEMENTS

The spectrometer used in this work was funded by the Science Research Council (U.K.). One of us (R.G.E.) would like to thank Wolfson College, Oxford, for the award of a Research Fellowship.

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27. The implication that $R_{t_{1u}\gamma_{u(5f)}} > R_{t_{1g}\gamma_{u(5f)}}$ may be rationalized in terms of the differing localization properties of t_{1g} and t_{1u} molecular subshells. In an LCAO model the t_{1g} orbitals are of essentially pure chlorine 3p atomic character; within the Xα framework the t_{1g} orbitals have no partial wave contribution from the uranium sphere. By contrast the t_{1u} shell can assume metal 5f and np (n = 6,7) character. Thus in terms of the formalism developed by Bird, et al.[28] $R_{t_{1g}\gamma_{u(5f)}}$ contains only two-center contributions whereas $R_{t_{1u}\gamma_{u(5f)}}$ has both one- and two-center contributions. One center Coulomb integrals are of course inherently larger than corresponding two center terms.

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Table I. Ionization energies and relative band intensities from the p.e. spectrum of UCl_6.

Band	Ionization Energy (eV)	Relative Intensity*			Assignment
		He(I)		He(II)	
a	11.28	3.0	(3)	3.0	$t_{1g}(\pi)$
b	11.74	3.1	(3)	3.3	$t_{1u}(\sigma+\pi)$
c	12.07	8.8	(7)	11.4	$t_{2u}(\pi)$
d	12.34(sh)				$t_{1u}(\sigma+\pi)$
	12.45				$a_{1g}(\sigma)$
e	13.28	5.2	(5)	5.9	$t_{2g}(\pi)$ + $e_g(\sigma)$

*Band intensities are normalized such that the intensity of band a is 3.0. Figures in parentheses give the normalized intensities expected on statistical grounds only.

Table II. A comparison between calculated and experimental ionization energies for UCl_6.

Subshell	Ionization Energy (eV)		Sphere Charge Distribution		
	Calculated	Experimental	$Q_{intersphere}$	Q_U	Q_{Cl}
t_{1g}	11.60	11.28	0.22	0.00	0.75
t_{1u}	11.76	11.74	0.16	0.21	0.60
t_{2u}	12.43	12.07	0.24	0.13	0.60
t_{1u}	12.68	12.34	0.22	0.21	0.54
a_{1g}	12.89	12.45	0.19	0.10	0.66
t_{2g}	13.16	13.28	0.33	0.06	0.60
e_g	13.46		0.13	0.18	0.66

Mean square deviation between experimental and calculated ionization energies is 0.29 eV.

Table III. Results of transition state calculations of charge transfer energies in UCl_6.

One-Electron Excitation Process	Energy (eV)
$t_{1g} \rightarrow a_{2u}$ (5f)	1.78
$t_{1g} \rightarrow t_{2u}$ (5f)	2.18
$t_{1g} \rightarrow t_{1u}$ (5f)	3.21
$t_{1u} \rightarrow a_{2u}$ (5f)	1.84
$t_{1u} \rightarrow t_{2u}$ (5f)	2.25
$t_{1u} \rightarrow t_{1u}$ (5f)	3.32

FIGURE CAPTIONS

Figure 1. The He-I and -II excited gas phase photoelectron spectra of UCl_6.

Figure 2. SCF-Xα scattered-wave ground state orbital energies for UCl_6. Solid lines represent occupied M.O.'s, dashed lines empty orbitals. The SCF-Xα orbital energies for U and Cl free atoms are also shown.

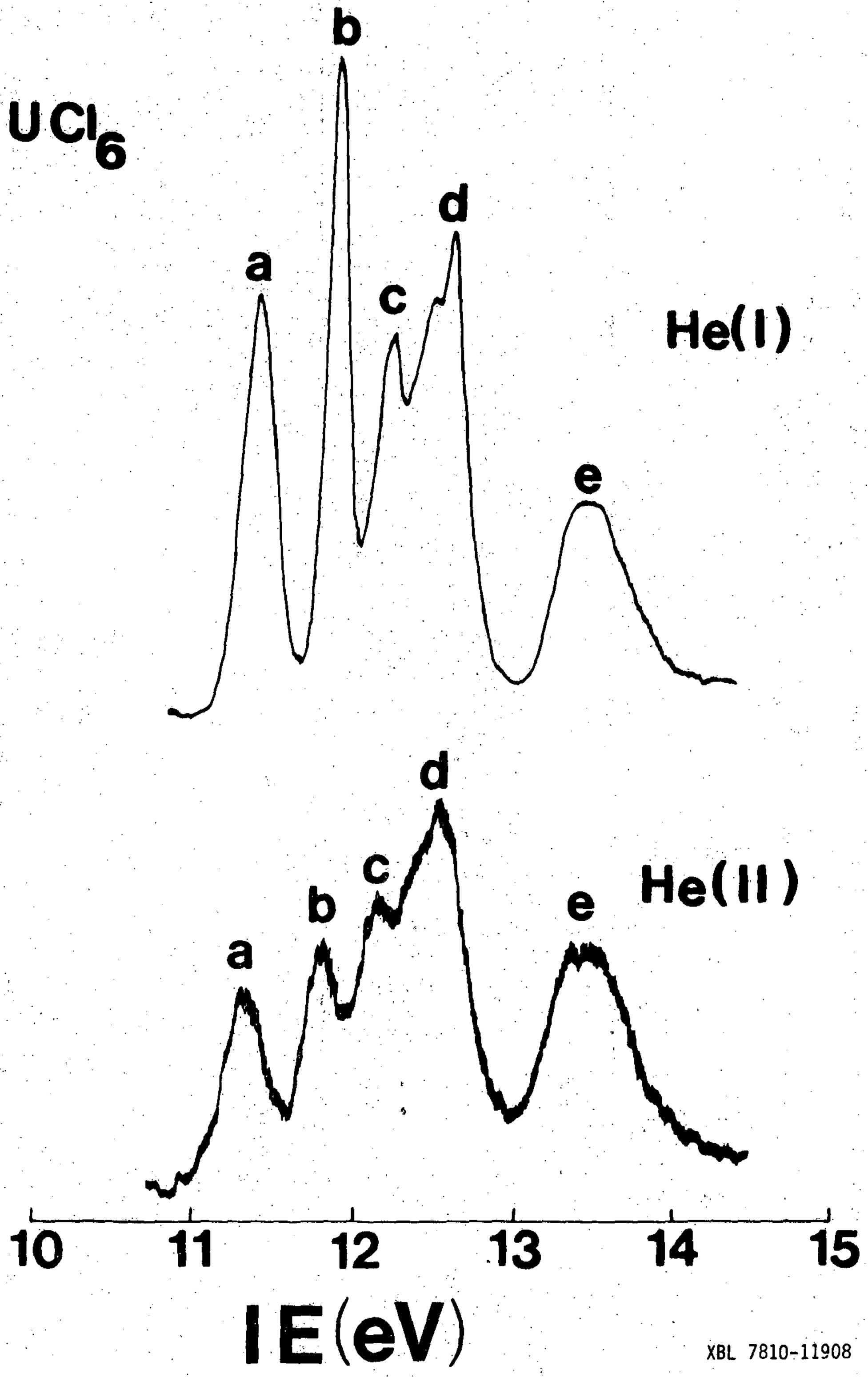

Figure 1

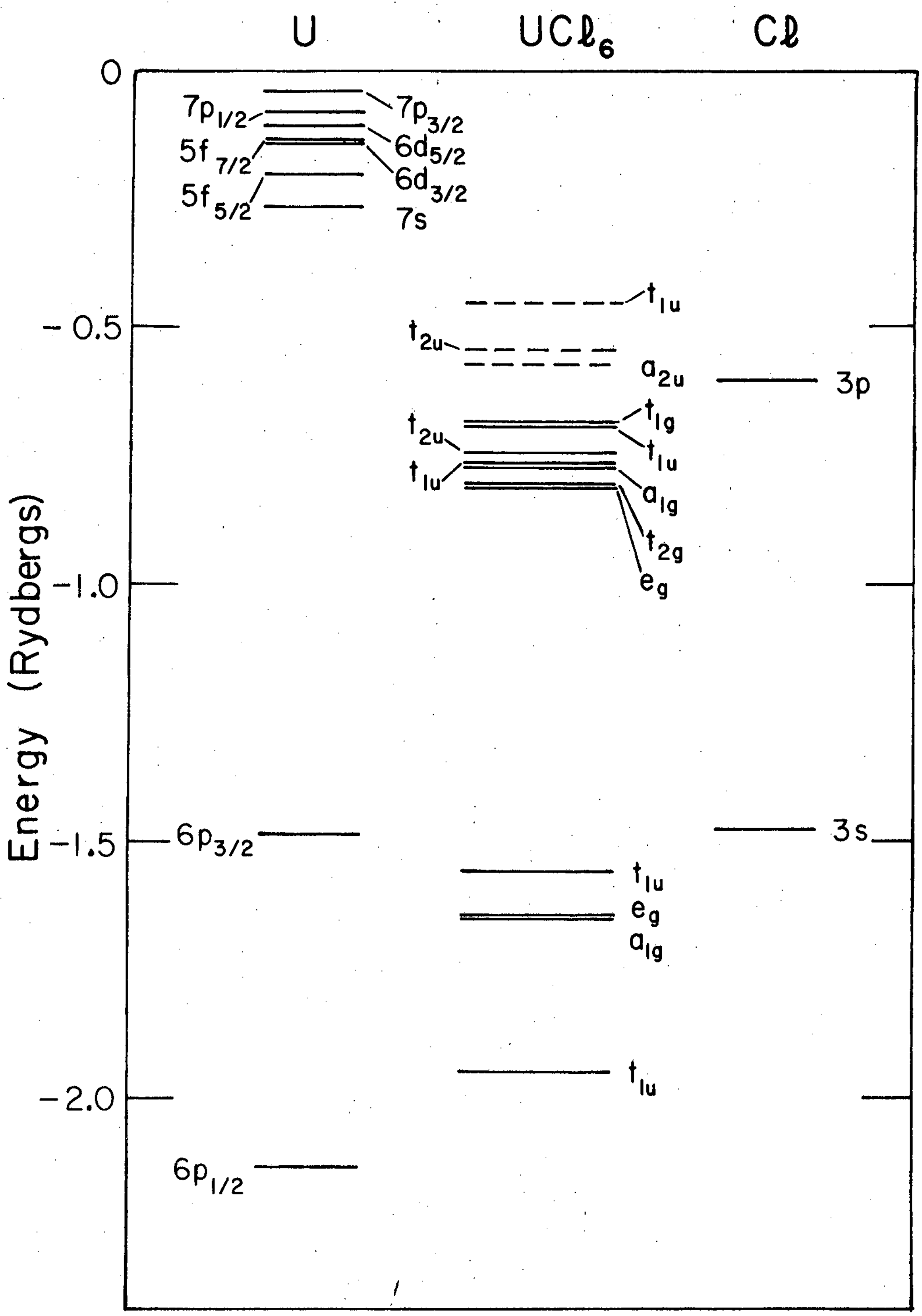

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Figure 2

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