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Close Correspondence between the Cs 4d Spectra of Molecular and Crystalline CsCl

by

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The Cs 4d absorption of molecular CsCl in the photon energy range from 70 eV to 180 eV has been determined for the first time. The absorption bands at the onset of the Cs 4d excitations are interpreted in terms of a simple ionic model. The close similarity of the spectrum of molecular and crystalline CsCl is discussed. The correspondence between these spectra and the 4d spectra of metallic and atomic Cs is pointed out.

Local effects often dominate the core spectra of solids[1]. The promising success of atomic or molecular approaches in the interpretation of the VUV spectra of crystalline alkali-halides[2,3] initiated the present investigation of the Cs 4d absorption of molecular CsCl.

The CsCl vapour (pressure 0.1 – 3 Torr) was contained in a high temperature furnace mounted in front of a 2m grazing incidence spectrograph (McPherson 247). The synchrotron radiation of the 7.5 GeV electron synchrotron DESY, transmitted through the vapour column, was registered on

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photographic plates bent along the Rowland circle. Details of the experimental arrangement are given elsewhere[4].

The 4d-absorption spectrum of molecular CsCl in the energy range from 70 eV to 180 eV is presented in Fig. 1, together with the 4d spectra of crystalline CsCl[5], Cs metal[6], and atomic Cs[7]. There is a marked similarity between the four spectra. They are all dominated by a strong, approximately 30 eV wide maximum, peaking between 100 eV and 110 eV. Transitions of the Cs 4d electrons to f-symmetric final states are responsible for this maximum[8]. A potential barrier suppresses these transitions at threshold and shifts the oscillator strength towards higher energies. For atomic Cs the theoretical cross section obtained within the random phase approximation with exchange (RPAE)[9] are in good agreement with the experimental results. The cross section due to transitions from outer subshells, the 4d cross section and the total cross section reported by Amusia[9] are included in Fig. 1. Due to the neglect of relaxation effects the theory predicts a higher 4d threshold energy and a steeper rise of the cross section above the 4d threshold than determined experimentally.

All spectra show structure superimposed on the rising continuum absorption between 84 eV and 100 eV. The one to one correspondence of the peaks E, F, G and H in the spectra of molecular and solid CsCl indicates a common origin and a highly localized character of these excitations. The simultaneous excitation of one 4d and one 5p electron is responsible for the fine structure detected between 92 eV and 102 eV in the spectrum of atomic Cs[7]. Double excitations of this type are probably responsible for the maxima G and H in the spectra of molecular and crystalline CsCl and for the shoulder G in the spectrum of metallic Cs. Transitions from the Cs 4p level give rise to the maxima detected at 160 eV.

Figure 2 shows the spectra at the onset of the Cs 4d transitions in molecular and crystalline CsCl, in Cs metal and in atomic Cs in an enlarged scale. In atomic Cs the transitions Cs $4d^{10}5s^25p^66s \rightarrow$ Cs $4d^95s^25p^66s6p$ give rise to the two groups of lines B and C. The groups are separated by the spin orbit splitting (2.2 eV) of the Cs 4d core[7]. Each group consists of three lines split by the interaction of the 6s6p electrons. Except for the terms $F_o(4d6s)$ and $F_o(4d6p)$ the interaction of the outer 6s and 6p electrons with the 4d hole is too small to cause any multiplet splitting detectable in the spectra[7]. Starting from these findings and taking into account the ionic character of the bond we ascribe the maxima $B_{\pi,\sigma}$ and $C_{\pi,\sigma}$ of molecular CsCl to the transitions Cs^+ $4d^{10}5s^25p^6 \rightarrow Cs^+$ $4d^95s^25p^66p$. The fact, that transitions from the Cs 4d level only probe those parts of the final orbitals close to the nucleus support the interpretation in terms of transitions of the Cs^+ ion. The molecular field splits the 6p level into a σ and a π component. The σ component is raised in comparison to the π component by the stronger repulsion by the Cl^- ion. The intensity ratios B_π/B_σ and C_π/C_σ support the assignment of the low energy component to π. The Z+1 analog[4] to CsCl with a Cs 4d core hole is BaCl. The lowest Ba 6s excitation in BaCl is very likely to be responsible for the C $^2\Pi$ state[10]. This corroborates the ordering of the π and σ states given above. The separation of the pairs B_π-C_π and B_σ-C_σ is in agreement with the spin orbit splitting of the 4d core[7]. The small maximum A is ascribed to transitions of the Cs^+ 4d electrons to an orbital with Cs^+ 6s parentage. The corresponding transitions are parity forbidden in the atom but weakly allowed in the molecule.

Going from molecular CsCl to crystalline CsCl the maxima B_π, B_σ and C_π, C_σ coalesce into the bands B and C because the 6p level is split by the molecular field but unsplit in the cubic symmetry of the crystal. In accordance with the interpretation of the spectrum of molecular CsCl we ascribe A to transitions to states mainly originating from Cs^+6s and B and C to transitions to final states with Cs^+6p parentage.

By comparison to the density of states calculated by Kmetko[11], Petersen[6] could show that for metallic Cs the maxima B, C and D are due to transitions of the 4d electrons to p-symmetric final states also. For both crystalline CsCl and metallic Cs the separation of the maxima B and C is given by the spin orbit splitting of the 4d core.

The energy positions of the peaks B and C for molecular and crystalline CsCl and for solid and atomic Cs differ by more than 1 eV. In contrast to this the strong maximum E showing up in the spectra of molecular and crystalline CsCl and Cs metal only shifts by less than 0.5 eV. There is no corresponding peak in the spectrum of atomic Cs, only some less pronounced structures could be detected at the same energy. The insensitivity of peak E to the local environment leads us to tentatively ascribe the maximum E to transition to f symmetric final states localized within the potential barrier around the Cs core. The energy position of the Ba^{++} (Z+1 analog to core excited Cs^+) 4f and 5f levels relative to the position of the 6s and 6p level[12] supports this interpretation.

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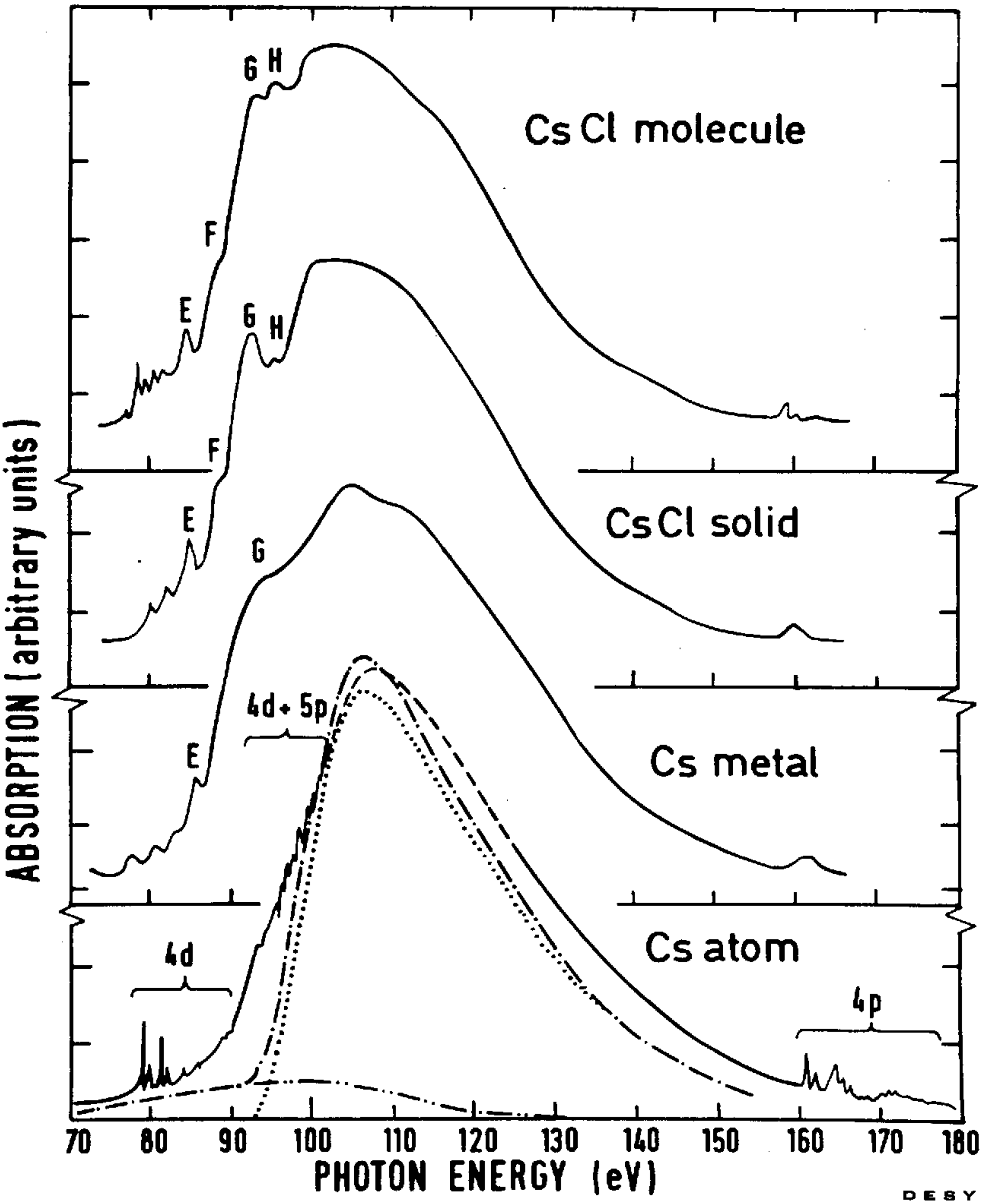
Figure Captions

Fig. 1 Cs 4d absorption spectra of molecular and crystalline CsCl, Cs metal and atomic Cs. The cross sections calculated by Amusia for the 4d absorption ••••••, for the contributions of the outer subshells -••-••-••- and the total cross section -•-•- are included.

Fig. 2 Absorption spectra at the Cs 4d threshold for molecular and crystalline CsCl, Cs metal and atomic Cs. The interpretation of the most prominent lines of atomic Cs and for molecular CsCl in the framework of the ionic model is indicated.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PHOTON ENERGY (eV)
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90
100
110
120
130
140
150
160
170
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Cs Cl solid
Cs metal
Cs atom
E
F
G
H
4d
4d + 5p
4p

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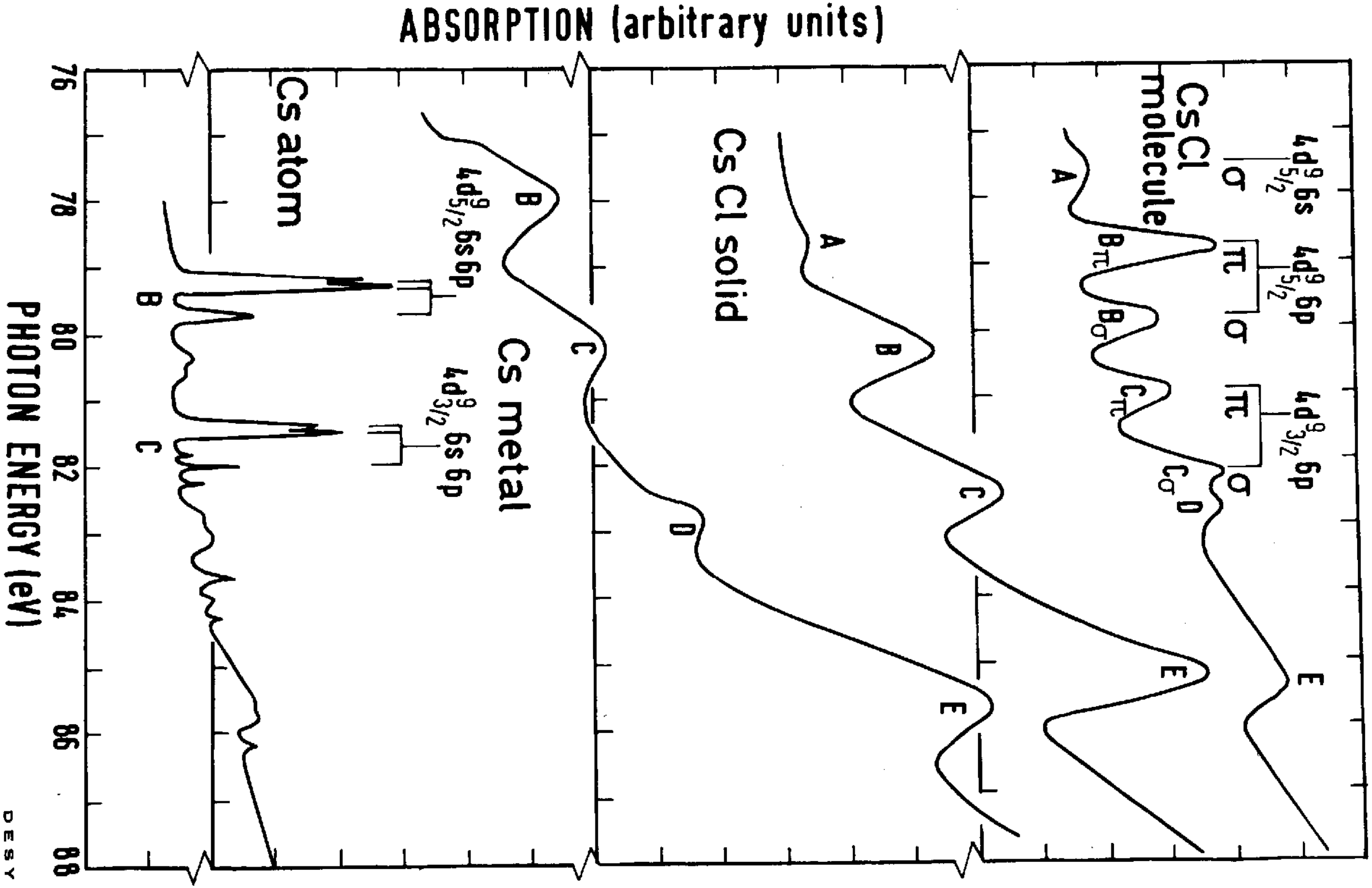
ABSORPTION (arbitrary units)
PHOTON ENERGY (eV)
76
78
80
82
84
86
88
Cs Cl molecule
$4d^9_{5/2}$ 6s
$4d^9_{5/2}$ 6p
$4d^9_{3/2}$ 6p
σ
π
σ
π
σ
A
B_π
B_σ
C_π
C_σ
D
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Cs Cl solid
A
B
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D
E
Cs metal
B
$4d^9_{5/2}$ 6s 6p
C
$4d^9_{3/2}$ 6s 6p
D
Cs atom
B
C

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