An *ab initio* Calculation of *K*-Spectra in Molecules HCl and HF

Lev N. Mazalov, Anatoly V. Kondratenko, Faris K. Gel'mukhanov, Vasily V. Murakhtanov and Tamara I. Guzhavina

Institute of Inorganic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 90, USSR

An *ab initio* calculation of energies and intensities of *K*-emission and *K*-absorption spectra in molecules HCl and HF are carried out. An electronic readjustment due to a hole in a molecular core is taken into account. A vibrational structure of *K*-emission and *K*-absorption spectra is also calculated. The calculation shows that it is possible to detect a vibrational structure of valence bonding levels in X-ray emission spectra. A good agreement with experiment is obtained.

Key words: X-ray spectrum of HCl and HF – Vibrational structure – HCl – HF

1. Introduction

The present paper deals with a calculation of energies and intensities of *K*-emission and *K*-absorption lines in two simple molecules. Different models are used to interpret X-ray spectra. *Ab initio* calculations are necessary to study the applicability of any model, to analyze the electronic structure of X-ray excited states and computational approximations. We used a one-center method offered in [1]. This method was successfully used for hydrides in [1].

2. One-Center Calculation

A wave function Ψ of an N-electron system can be written in the form of a Slater determinant ($h = m = e = 1$)

$$\Psi = \frac{1}{\sqrt{N!}} \det (\psi_1 \psi_2 \ldots \psi_N),$$

$$\psi_i = R_{nl}(r) Y_{lm}(\vartheta, \psi) S_{m_z}(\sigma),$$

$$R_{nl}(r) = \sum_{k=l}^{n-1} a_k r^k \exp(-\alpha_{nlmm_z} r).$$

(1)

Here Y_{lm} = spherical functions, S_{m_z} = spin functions, ψ_i = one-electron spin-orbitals in the form offered by Fock and Petrashen (FP function). The origin of the coordinate

system is placed at a "heavy" nucleus (Cl or F). Coefficients a_k are calculated from ortho-gonality conditions

$$\langle R_{nl} | R_{n'l} \rangle = \delta_{nn'}.$$

The parameters α are varied to obtain the best value of the energy of any state.

Intensities of transitions are calculated in accordance with

$$I \sim |\vec{W}_{ik}|^2, \qquad \vec{W}_{ik} = \langle \Psi_i | \sum_{j=1}^{N} \vec{r}_j | \Psi_k \rangle$$

$$= \begin{vmatrix} \vec{f}_{11} & f\vec{f}_{12} & \ldots & \vec{f}_{1N} \\ s_{21} & s_{22} & \ldots & s_{2N} \\ \ldots & \ldots & \ldots & \ldots \\ s_{N1} & s_{N2} & \ldots & s_{NN} \end{vmatrix} + \begin{vmatrix} s_{11} & s_{12} & \ldots & s_{1N} \\ \vec{f}_{21} & \vec{f}_{22} & \ldots & \vec{f}_{2N} \\ \ldots & \ldots & \ldots & \ldots \\ s_{N1} & s_{N2} & \ldots & s_{NN} \end{vmatrix} + \ldots, \tag{2}$$

where

$$s_{ab} = \langle \psi_a^i | \psi_b^k \rangle, \qquad \vec{f}_{ab} = \langle \psi_a^i | r | \psi_b^k \rangle.$$

Results of our calculations of energies and intensities of X-ray K-emission spectra in molecules HCl and HF are given in Table 1. The electronic readjustment due to a hole in a molecular core is taken into account when X-ray excited states are calculated. The K_β-line of HCl corresponds to the transitions $1s \leftarrow 3p_0$ (bonding level 5σ) and $1s \leftarrow 3p_\pm$ (unbonding level 2π) in the one-center method, the K_α-line of HF corresponds to the transitions $1s \leftarrow 2p_0$ (bonding level 3σ) and $1s \leftarrow 2p_\pm$ (unbonding level 1π).

Results of the calculation of energies and intensities of K-absorption lines in HCl and HF are given in Table 2. The electronic readjustment accompanying core ionizations in HCl and HF is also taken into account. Rydberg np-orbitals of the excited electron were constructed as linear combinations of p-symmetry FP functions with $n \geqslant n_p$, where

$$n_p = \begin{cases} 4 \text{ for HCl} \\ 3 \text{ for HF.} \end{cases}$$

Table 1. K-Emission spectra of molecules HCl and HF (Energy in eV, intensity in relative units)

Molecule	Transition	Our Calculation		Experiment [2][a]	
		Energy	Intensity	Energy	Intensity
HCl	$1s \leftarrow 3p_\pm$	3.35	3.2	3.5 ± 0.1	4.3 ± 0.1
	$1s \leftarrow 3p_0$	0	1	0	1
HF	$1s \leftarrow 2p_\pm$	3.4	2.7	–	–
	$1s \leftarrow 2p_0$	0	1	–	–

[a] Experimental data in the maxima of the spectrum.

Table 2. K-absorption spectra of molecules HCl and HF (Energy in eV from the continuous edge, intensity in relative units)

Molecule	Transition	Our Calculation		Experiment [2]	
		Energy	Intensity	Energy	Intensity
HCl	$1s \leftarrow \psi_a(6\sigma)$	6.05	1.8	6.1 ± 0.1	1.55 ± 0.1
	$1s \rightarrow 4p$	2.55	1	2.2 ± 0.2	1
	$1s \rightarrow 5p$	1.2	0.4	0.7^{a}	0.6^{a}
HF	$1s \rightarrow \psi_a(4\sigma)$	6.9	4.1	–	–
	$1s \rightarrow 3p$	3.0	3.2	–	–
	$1s \rightarrow 4p$	1.4	1	–	–

[a] An estimate.

The Rydberg orbitals are orthogonal to one another. They are also orthogonal to occupied p-symmetry orbitals.

The vacant antibonding molecular orbitals ψ_a were constructed as linear combinations of s, p, d symmetry FP functions.

$$\psi_a = -0.560\ 4p_0\ (0.95) \quad -0.237\ 5p_0\ (1.35) \quad -0.036\ 6p_0\ (2.7) \quad + 0.636\ 4s\ (1.3)$$
$$+ 0.075\ 5s\ (2.4) \quad -0.462\ 3d_0\ (0.8) \quad -0.073\ 4d_0\ (0.8)$$

for HCl and

$$\psi_a = -0.594\ 3p_0\ (1.1) \quad -0.063\ 4p_0\ (1.96) + 0.728\ 3s\ (1.04) + 0.128\ 4s\ (1.66)$$
$$+ 0.017\ 5s\ (3.16) + 0.312\ 3d_0\ (1.04)$$

for HF.

Parameters α for the FP functions are given in parentheses. A complicated form of ψ_a means that ψ_a are molecular orbitals. On the other hand similar orbitals are constructed from FP functions with the same quantum number l. It means that they are of the Rydberg type.

Our results are in good agreement with the experimental data for K-spectra of a molecule HCl. We do not know the experimental data for molecule HF.

3. Vibrational Fine Structure

The vibrational fine structure of lines in X-ray spectra of HCl and HF was calculated

in the one-particle harmonic approximation proposed in [3, 4]. In this approximation the model Hamiltonian of a molecule has the form [4]

$$H = \sum_i \epsilon_i(Q_0) a_i^+ a_i + \sum_s w_s(b_s^+ b_s + 1/2)$$

$$+ \sum_s \sum_i 2^{-1/2} \left(\frac{d\epsilon_i}{dQ_s}\right)_0 (a_i^+ a_i - n_i)(b_s^+ + b_s) \tag{3}$$

$$+ \sum_{ss'} \sum_i 1/4 \left(\frac{d^2\epsilon_i}{dQ_s dQ_{s'}}\right)_0 (a_i^+ a_i - n_i)(b_s^+ + b_s)(b_{s'}^+ + b_{s'}),$$

where i labels the one-electron orbitals, s designates the dimensionless normal coordinates Q. Q_0 is the equilibrium geometry of the molecule on the Hartree–Fock level. The a_i^+ and b_s^+ are the creation operators associated with the electronic orbitals and vibrational quanta, respectively. $n_i = 1$ if i is an occupied orbital and $n_i = 0$ if i is a vacant orbital in the Hartree–Fock ground state, w_s are the Hartree–Fock frequencies.

Intensity of the X-ray emission spectrum is defined by

$$I(w') = \int \sigma_E(w', W) J(w) \, dw, \tag{4}$$

where w and w' are the initial and final photon frequency, respectively. $J(w)$ is the spectral function of an excited radiation. A photon-molecule inelastic scattering cross-section $\sigma_E(w', w)$ is given by [3]

$$\sigma_E(w', w) \sim \sum_f \left| \sum_n \frac{\langle f|V^+|n\rangle\langle n|V|0\rangle}{w - w_{n0} + i\frac{\Gamma_n}{2}} \right|^2 \delta(w - w' - w_{f0}). \tag{5}$$

The absorption cross-section $\sigma_A(w)$ may be written as

$$\sigma_A(w) \sim \sum_n |\langle n|V|0\rangle|^2 \frac{\Gamma_n/2\pi}{(w - w_{n0})^2 + \Gamma_n^2/4}. \tag{6}$$

In Eqs. (5) and (6)

$$w_{n0} = E_n - E_0.$$

E_n and $|n\rangle$ are the energy eigenvalues and eigenstates of a molecular Hamiltonian H. Γ_n^{-1} is the lifetime of the intermediate X-ray excited state $|n\rangle$. The coupling of electrons to the initial (final) photon is described by the usual semi-classical Hamiltonian $V(V')$

$$V = \sum_{ki} V_{ki} a_k^+ a_i.$$

Using Born–Oppenheimer approximation and one-particle harmonic approximation
the cross-sections (5) and (6) may be written as (for diatomic molecule)

$$\sigma_E(w', w) \sim \sum_{ik}^{occ.} |\vec{W}_{i0}|^2 |\vec{W}_{ki}|^2 \sum_{\hat{n}_k} \delta(w' - w - \epsilon_k + w^k(n_k + 1/2) - f^{k^2} w^k)$$

$$\times \left| \sum_{\hat{n}_i} \frac{\langle \hat{n}_k | \hat{n}_i \rangle \langle \hat{n}_i | \hat{0} \rangle}{[w' - (-\epsilon_i + w^i(n_i + 1/2) - f^{i^2} w^i + \epsilon_k - w^k(n_k + 1/2) + f^{k^2} w^k] + i\dfrac{\Gamma_n}{2}} \right|^2$$

$$= G(w') + IG(w') \tag{7}$$

and

$$\sigma_A(w) \sim \sum_{i}^{occ.} \sum_{\nu}^{vac.} [\vec{W}_{\nu i, 0}]^2 \sum_{\hat{n}_{\nu i}} |\langle \hat{n}_{\nu i} | \hat{0} \rangle|^2$$

$$\times \frac{\Gamma_n/2\pi}{[w - (\epsilon_\nu - \epsilon_i + w^{\nu i}(n_{\nu i} + 1/2) - f^{\nu i^2} w^{\nu i})]^2 + \Gamma_n^2/4}. \tag{8}$$

Equation (7) describes the two electronic transitions $i \to \nu$, $k \to i$, and Eq. (8) corresponds to electronic transition $i \to \nu$. $G(w')$ is the leading term of inelastic scattering contribution from different channels, $IG(w')$ describes the interference between vibrational states $|\hat{n}_i\rangle$ of the intermediate electronic state i. The superscripts occ. and vac. refer to summations over all occupied and unoccupied orbitals in the Hartree–Fock ground state, respectively. Summing over i, k and ν is defined by the frequencies w and w'. w_0 is the vibrational frequency of the ground state on the Hartree–Fock level.

$|\langle \hat{n}_i | \hat{0} \rangle|^2$ and $|\langle \hat{n}_k | \hat{n}_i \rangle|^2$ are the usual Franck–Condon factors. $w^{\nu i}$ and $n_{\nu i}$ are the vibrational frequency and quantum number of the excited state with the hole in shell i and an excited electron at orbital ν, respectively:

$$w^{\nu i} = w_0 \left(\frac{w_0 + 4\gamma^{\nu i}}{w_0} \right)^{1/2},$$

$$f^{\nu i} = \frac{g^{\nu i}}{w_0} \left(\frac{w_0}{w_0 + 4\gamma^{\nu i}} \right)^{3/4},$$

$$g^{\nu i} = 2^{-1/2} \left(\frac{d(\epsilon_\nu - \epsilon_i)}{dQ} \right)_0,$$

$$\gamma^{\nu i} = 1/4 \left(\frac{d^2(\epsilon_\nu - \epsilon_i)}{dQ^2} \right)_0. \tag{9}$$

For the intermediate state with the hole in a shell i

$$w^i = w_0 \left(\frac{w_0 + 4\gamma^i}{w_0} \right)^{1/2}, \qquad \gamma^i = -1/4 \left(\frac{d^2\epsilon_i}{dQ^2} \right)_0,$$

and so forth.

There is a simple relation between f^i and the shift of the equilibrium geometry of a molecule due to the excitation process (for diatomic molecule)

$$\Delta R = -(2)^{1/2} \frac{f^{vi}}{(\mu w^{vi})^{1/2}}, \tag{10}$$

where μ is a reduced mass of a molecule.

One can easily see from the equations for calculating vibrational fine structure of the spectra that it is not necessary to compute potential curves of excited states. It is the chief advantage of this method in comparison with traditional procedures.

The calculated forms of the K-emission and absorption spectra of HCl and HF are displayed in Figs. 1–4. The intensity of the X-ray spectra in all figures has arbitrary units. The parameters g^i and γ^i for occupied orbitals i are calculated from the Hartree-Fock data of Cade and Huo [5]. CNDO/BW [6] calculations have been carried out on HCl and HF to obtain derivatives $(d\epsilon^v/dR)_0$ and $(d^2\epsilon^v/dR^2)_0$ for vacant orbitals (6σ for HCl and 4σ for HF).

There is a relation between parameters f^{1s} and $f^{n\sigma}$ in molecules HCl and HF, $f^{1s} \ll f^{n\sigma}$, where $n\sigma$ labels the valence bonding orbitals. As was shown in [3] in this case the vibrational fine structure in X-ray emission spectra is similar to the vibrational fine structure in the photoelectron spectra of the corresponding valence orbitals [7].

The calculated vibrational fine structure of the K-absorption spectra of HCl and HF are given in Figs. 3 and 4. The changes of the interatomic distance due to excitation of the $1s$-electron to vacant orbitals for HCl ($Cl\,1s \rightarrow 6\sigma$) and HF ($F\,1s \rightarrow 4\sigma$) are 0.235 and 0.211 (a.u.). Taking into account that for HCl and HF $f^{1s} \approx 0$ and Eqs. (9) and (10) it is
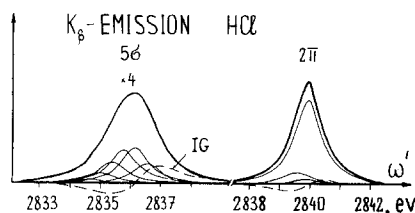
Fig. 1. The calculated HCl X-ray K_β-emission spectrum. The thin solid lines represent vibrational components and the dotted interference term IG (see text). The vibrational frequency in the ground state w_0 is 0.39 eV, linewidth Γ is 1.1 eV
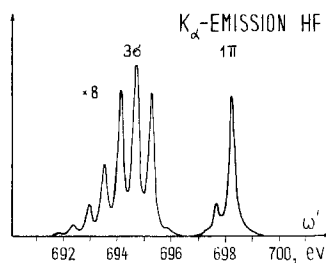
Fig. 2. The calculated HF X-ray K_α-emission spectrum. An interference term is negligible. The vibrational frequency in the ground state is 0.55 eV, linewidth Γ is 0.22 eV

K-ABSORPTION HCl

Cl 1s-6δ

2851   2854   2857, eV
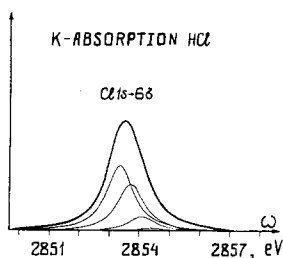
K-ABSORPTION HF

F1s – 4δ

714   717   720, eV

Fig. 3. The calculated absorption cross-section of K excitation for HCl showing four vibrational components separated by 0.36 eV. Linewidth Γ is 1.1 eV
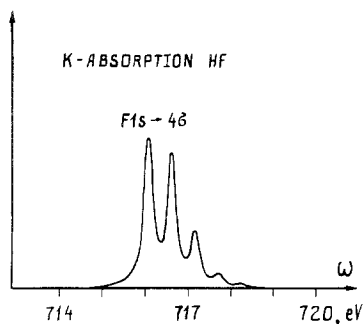
Fig. 4. The calculated absorption cross-section of K excitation for HF showing five vibrational components separated by 0.54 eV. Linewidth Γ is 0.22 eV

clearly evident that vacant molecular orbitals 6σ in HCl and 4σ in HF have anti-bonding character. Furthermore, the anti-bonding character of the 6σ orbital in HCl was discussed by W. H. E. Schwarz in [8], where the *ab initio* calculation of the L-absorption spectrum of HCl was carried out.

Unfortunately, the high resolution K_β-emission and K-absorption spectra of HCl and X-ray spectra of HF are not yet known.

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