First-Principles Analysis of the Rb_2CrF_6 Absorption Spectrum

Mikhail G. Brik

Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan

Reprint requests to Dr. M.G. B.; E-mail: brik@fukui.kyoto-u.ac.jp and brik@ksc.kwansei.ac.jp

Z. Naturforsch. **61a,** 293 – 298 (2006); received February 27, 2006

A systematic first-principles analysis of the energy level scheme and absorption spectrum of Cr^{4+} in Rb_2CrF_6 crystal is presented. The recently developed first-principles approach to the analysis of the absorption spectra of ions in crystals based on the discrete variational multi-electron (DV-ME) method was used in the calculations. The method is based on the numerical solution of the Dirac equation and has a wide area of applicability. As a result, the complete energy level scheme of Cr^{4+} and its absorption spectrum were calculated, assigned and compared with available experimental literature data on the ground state absorption. Numerical contributions of all possible electron configurations to the wave functions of the calculated states were determined. By analysing the molecular orbitals population, numerical contributions of the fluorine 2p- and 2s-orbitals to the 3d-molecular orbitals were determined. The significant contribution of the ligand's wave functions shows the high degree of covalency in the considered crystal. – PACS numbers: 71.70.Ch, 71.70.Ej

Key words: First-Principles Calculations; Crystal Field Theory; 3d-Ions; Ground State Absorption.

1. Introduction

The ion Cr^{4+} is widely used for getting tunable lasers in the infra-red region; many studies devoted to this ion have been published during the last 10 – 15 years (see, for example, recent reviews [1, 2] and references therein). In most papers published on this subject Cr^{4+} is treated as an impurity to the host crystal. The number of studies devoted to crystals containing Cr^{4+} not as an impurity but as an intrinsic ion is significantly smaller. The reason is that Cr^{4+} is difficult to obtain, especially in fluoride lattices. Rb_2CrF_6 crystal was studied experimentally in [3]; *ab initio* calculations of the Cr^{4+} absorption spectrum in the same host were reported in [4 – 6]. This host is of special interest, since Cr^{4+} is 6-fold coordinated. This is a rather rare case (in doped crystals Cr^{4+} exhibits a preference to occupy tetrahedral sites [1]), therefore, this crystal is a good system to study the energy levels of Cr^{4+} in octahedral environment.

As pointed out in [6], in [5] there exists an ambiguity in calculating the Cr^{4+} energy levels in Rb_2CrF_6 and relating them to the experimental data from [3]. In particular, the absorption band at around 20200 cm^{-1} observed in [3] and assigned to the $^3T_{1g}(^3F) - {}^3T_{2g}(^3F)$ transition of Cr^{4+} was not reproduced theoretically in [5]. The question did also arise whether in [5] it is reasonable to take the Cr–F distance as 1.72 Å, since the splitting of the ^3F term (the ground term of the Cr^{4+} ion) depends strongly on the interionic separation. The low-lying energy levels of Cr^{4+} were obtained in [6] with thorough and rigorous consideration of different embedding effects and geometry optimization [7, 8]; a comparison of the obtained energy levels with the experimental spectrum was discussed and the conclusion was made that the actual Cr–F distance in Rb_2CrF_6 is greater than 1.800 Å. The energy level at 22090 cm^{-1} obtained in [6] was assigned to the above-mentioned $^3T_{1g}(^3F) - {}^3T_{2g}(^3F)$ transition, though the overestimation of its position in comparison with experimental results [3] is about 2000 cm^{-1}. That is why in the present paper an attempt is made to clarify these questions by using a quite different approach, based on the recently developed discrete variational multi-electron (DV-ME) method [9].

The aim of the present study is to calculate the complete energy level scheme and absorption spectrum of Cr^{4+} in the considered host, compare it with experimental values [3] and results of theoretical calculations [5, 6], and estimate numerically the covalency effects. It is demonstrated that it is possible to get a reasonable agreement between the experimental and calculated energy levels and absorption spectra using the

literature data on the Cr–F distance, which is smaller than 1.8 Å.

2. Crystal Structure and Experimental Spectroscopic Data of Rb_2CrF_6

The crystal structure of Rb_2CrF_6 is described in [10, 11]. It crystallizes in the cubic $Fm3m$ group (space group number 225) with the lattice constant $a = 8.523$ Å. The Cr^{4+} ion is surrounded by six F^- ions forming an ideal octahedron with a Cr–F bond length of 1.722 Å [10, 11]. The diffuse reflectance spectrum of Rb_2CrF_6 recorded in [3] shows a prominent band at 20200 cm^{-1} ascribed to the first spin-allowed transition $^3T_{1g}(^3F) - {}^3T_{2g}(^3F)$. The $^3T_{1g}(^3F) - {}^3T_{1g}(^3P)$ transition in [3] was given the energy value 28400 cm^{-1}. The spin-allowed transition $^3T_{1g}(^3F) - {}^3A_{2g}(^3F)$ was not detected in [3]. A weak spin-forbidden transition at 11400 cm^{-1} was assigned to the $^3T_{1g}(^3F) - {}^1E_g$, $^1T_{2g}(^1D)$ transitions. From the experimental positions of the absorption bands the authors of [3] obtained the values of the Racah parameter B and crystal field strength Dq as (680 ± 80) cm^{-1} and (2170 ± 10) cm^{-1}, respectively. The Racah parameter C was not estimated in [3]; the authors of [4] reported the energy levels calculations with different values of C, from 2960 to 3880 cm^{-1} (with different approximations involved).

3. Method of Calculations

We apply the fully-relativistic discrete variational multi-electron (DV-ME) method, which is a configuration-interaction (CI) calculation program using the four-component fully-relativistic molecular spinors obtained by the discrete-variational Dirac-Slater (DV-DS) cluster calculations, developed by Ogasawara et al. [9]. The method is based on the numerical solution of the Dirac equation, and its main advantages are as follows: 1.) A first-principles method is applied without any phenomenological parameters (this is especially important for the development of new materials, prediction of their expected properties and analysis of the existing trends between similar compounds); 2.) a wide area of applications, in principle to any atom or ion in any symmetry from spherical to C_1 for any energy interval from IR to X-ray; 3.) the possibility to take into account all effects of chemical bond formation, exchange and configuration interaction by means of numerical integration; 4.) the potential to model optical properties of solids by calculating optical transition probabilities using the obtained wave functions. All relativistic effects, such as spin-orbit interaction and dependence of mass on velocity, are no longer considered as small perturbations, but are taken into account from the very first step of the calculations. The key idea of the method is that the molecular orbitals (MO) consisting of the wave functions of an impurity ion and ligands are used throughout the calculations rather than the atomic wave functions. Since the percentage contribution of wave functions of different ions to any MO can be readily evaluated, this allows the effects of covalency to be taken into account explicitly. The many-electron wave functions are expressed as linear combination of the MO-based Slater determinants and the absorption peak assignment can be done in terms of these Slater determinants. The relativistic many-electron Hamiltonian is written (in atomic units) as

$$H = \sum_{i=1}^{n} \left[c\boldsymbol{\alpha}\mathbf{p}_i + \beta c^2 - \sum_{\nu} \frac{Z_\nu}{|\mathbf{r}_i - \mathbf{R}_\nu|} + V_0(\mathbf{r}_i) + \sum_{\mu} \frac{Z_\mu^{\mathrm{eff}}}{|\mathbf{r}_i - \mathbf{R}_\mu|} \right] + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1)$$

where $\boldsymbol{\alpha}$, β are the Dirac matrices, c the velocity of light, $\mathbf{r}_i$, $\mathbf{p}_i$ the position and the momentum operator of the ith electron, Z_ν and $\mathbf{R}_\nu$ the charge and position of the νth nucleus, Z_μ^{eff} and $\mathbf{R}_\mu$ the effective charge and position of the μth ion outside the model cluster, n the number of explicitly treated electrons (in our case, 3d-electrons of Cr^{4+}). $V_0(\mathbf{r}_i)$ is the potential from the remaining electrons [12]:

$$V_0 = \int \frac{\rho_0^{\mathrm{G}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}' + \frac{3}{4} \left\{ \left[\rho^{\mathrm{G}}(\mathbf{r}) V_{xc} \left\{ \rho^{\mathrm{G}}(\mathbf{r}) \right\} - \rho_0^{\mathrm{G}}(\mathbf{r}) V_{xc} \left\{ \rho_0^{\mathrm{G}}(\mathbf{r}) \right\} \right] \cdot \rho_1^{\mathrm{G}}(\mathbf{r})^{-1} - V_{xc} \left\{ \rho_1^{\mathrm{G}}(\mathbf{r}) \right\} \right\}, \quad (2)$$

where ρ^{G}, ρ_1^{G}, ρ_0^{G} represent the charge density of all electrons, that of the explicitly treated electrons and that of the remaining electrons, respectively, and V_{xc} is Slater's X_α potential. The superscript G indicates the values for the ground state. All matrix elements of the Hamiltonian (1) are calculated by numerical integration; diagonalization of the Hamiltonian (1) gives a complete electron energy level scheme for the considered cluster. Since the eigenfunctions are also ob-

Table 1. Observed [3] and calculated ([5], [6], and this work) energy levels (in cm^{-1}) of Cr^{4+} ion in Rb_2CrF_6.

Energy levels	Observed [3]	Calculated [5]	Calculated ([6], for two Cr – F distances)		Calculated (this work, without scaling factor)	Calculated (this work, with scaling factor)	Contribution (in %) of possible electron configurations		
			1.72 Å	1.80 Å			$\left(t_{2g}^2\right)$	$\left(t_{2g}^1 e_g^1\right)$	$\left(e_{2g}^2\right)$
$^3T_{1g}$	0	0	0	0	0	0	98.46	1.54	0.00
$^1T_{2g} + {}^1E_g$	11400	11004, 11250	12000, 12650	12140, 12810	12273	8799	99.35	0.57	0.08
$^1A_{1g}$	–	21539	27050	27020	28101	20146	96.42	0.01	3.57
$^3T_{2g}$	20200	26978	26685	22090	28792	20641	0.00	99.99	0.01
$^3T_{1g}$	28400	34263	36385	31720	40278	28875	1.54	98.46	0.00
$^1T_{2g}$	–	–	–	–	41544	29783	0.94	99.06	0.00
$^1T_{1g}$	–	–	–	–	45802	32835	0.00	100.0	0.00
$^3A_{2g}$	–	–	–	–	58980	42283	0.00	0.00	100.0
^1E_g	–	–	–	–	73201	52478	0.20	0.00	99.80
$^1A_{1g}$	–	–	–	–	89366	64066	3.57	0.00	96.43

tained, the absorption spectra (for electric dipole, electric quadrupole, and magnetic dipole transitions) can be obtained in a straightforward manner after calculating appropriate matrix elements. For example, in the case of electric dipole transitions the oscillator strength (averaged over all possible polarizations) is calculated as

$$I_{\mathrm{if}} = \frac{2}{3}(E_{\mathrm{f}} - E_{\mathrm{i}}) \left| \langle \Psi_{\mathrm{f}} | \sum_{k=1}^{n} \mathbf{r}_k | \Psi_{\mathrm{i}} \rangle \right|^2 , \qquad (3)$$

where Ψ_{i} and Ψ_{f} are the initial and final states with energies of E_{i} and E_{f}, respectively. To emphasize the wide applicability of the method employed in the present paper, we mention that it has been successfully applied to analyse the Cr^{4+} absorption spectrum of $Y_3Al_5O_{12}$ [13] and silicate crystals [14], the 4f–4f absorption spectrum of $LiYF_4$:Dy^{3+} [15], the 4f–5d absorption spectra of various trivalent lanthanides in $LiYF_4$ [16, 17], the high lying 4f and 5d energy states of free trivalent lanthanides [18, 19], and to calculate the X-ray absorption near edge structure (XANES) spectra of transition metal ions [20 – 22].

It should be mentioned here that there exists an overestimation (by about 20 – 30%) of the energy levels obtained using the DV-ME method. This overestimation is due to underestimation of the electron correlation [17, 18]. This discrepancy can be decreased by including into the basis set the high-lying electron configurations, but this would lead to a significant increase of the dimension of the Hamiltonian matrix and computation time. In the next section the way to improve this trend will be suggested.

4. Results of Calculations and Discussion

An octahedral $[CrF_6]^{2-}$ model cluster was used for the calculation of energy levels and absorption spectra. The Cartesian coordinates of ions (in Å) in this cluster were obtained by using the crystal structure data from [10, 11]; six fluorine ions form an ideal octahedron around a Cr^{4+} ion with the $Cr^{4+} - F^-$ distance 1.72165 Å. In order to take into account the effects of the surroundings of the above model clusters, an effective Madelung potential was considered by locating several thousand point charges (with charges "+1" for Rb, "+4" for Cr, and "−1" for F) at atomic sites outside the cluster. The number of the sampling points for numerical integration was 100000, and the atomic orbitals used for the relativistic DV-Xα calculation were from 1s to 4p for Cr^{4+} ions and from 1s to 2p for F^- ions.

In an octahedral crystal field the 3d-orbitals are split into t_{2g} and e_g orbitals, with the former being the ground state and the latter situated above it by $10Dq$ [23]. Two d-electrons of the Cr^{4+} ion can be arranged in these orbitals as follows: $(t_{2g}^2 e_g^0)$, $(t_{2g}^1 e_g^1)$, and $(t_{2g}^0 e_g^2)$. The number of Slater determinants for each configuration is 15, 24, and 6, respectively. The Hamiltonian (1) was diagonalized in the space spanned by all 45 Slater determinants from the above given electron configurations; this ensured the proper taking into account the configuration interaction between possible electron configurations.

The results of the energy level calculations, in comparison with experimental results [3] and other calculations [5, 6] are shown in Table 1.

As was mentioned at the end of the previous section, the calculated energy levels are overestimated (Table 1, sixth column). Regarding the overestimation of the calculated energy levels, one can a posteriori introduce a scaling factor which minimizes the root-mean squared deviation between the calculated and experimental results. However, if only the *relative* positions of the energy levels and absorption bands in the calculated absorption spectrum are considered, this overestimation can be left out of consideration, because the whole spectrum is just shifted towards higher energies [17]. If, on the contrary, the *absolute* positions of the energy levels are to be defined more precisely, the scaling factor will scale down the calculated energy levels and bring them close to the observed ones without affecting the wave functions of the calculated energy levels. Such minimization was performed for experimental and calculated energy level sets, and the scaling factor was found to be 0.7169. The "scaled" energy level sets, obtained by multiplication of the numbers in the sixth column of Table 1 by the above factor (only the energy levels were multiplied by these factors, the corresponding eigenfunctions were not modified), are shown in the seventh column.

As can be seen from Table 1, agreement between the "scaled" calculated and measured energy levels is quite reasonable. Partial contributions (in %) of all possible electron configurations into the wave functions of the corresponding levels are also shown in Table 1 (the last three columns). It is interesting to note that there is almost no mixture between different configurations. This situation is opposite to the case of tetrahedrally coordinated Cr^{4+} (for example in $Y_3Al_5O_{12}$), where the spin-triplet states $^3T_1(^3F)$ and $^3T_1(^3P)$ were mixed with a ratio near to 1 : 1 [24].

Figure 1 shows the calculated and experimental absorption spectra of the octahedrally coordinated Cr^{4+} ions in Rb_2CrF_6. The calculated spectrum was obtained using (3); the computed "stick" spectra were then broadened by a Gaussian function. The experimental spectrum in [3] was recorded at 273 K and expressed in terms of the Kubelka-Munk function $F(R) = \frac{k}{s}$, where k is the absorbance coefficient and s is the scattering coefficient [25, 26]. Both spectra were normalized to unity for easiness of the comparison. The calculated spectrum (Fig. 1) reproduces the shape of the observed one, including the positions of the bands and their relative intensities (if the scaling factor is taken into account). The spin-forbidden $^3T_{1g} - {}^1E_g$, $^1T_{2g}$ absorption band is shown in the inset of Figure 1.

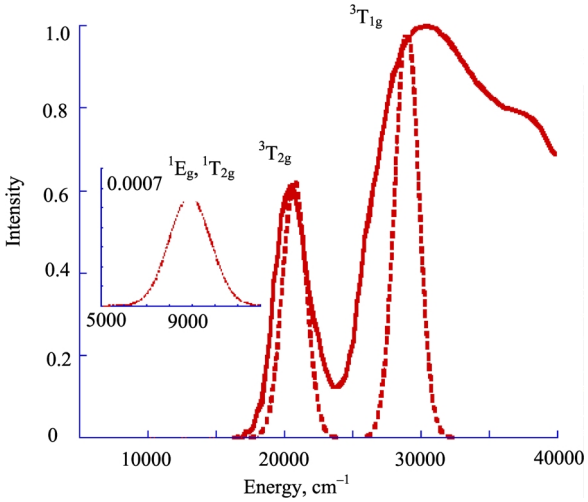

Fig. 1. Calculated (this work, dashed line) and observed reflectance spectrum ([3], solid line) of Rb_2CrF_6 (from 5000 to 40000 cm^{-1}). The inset shows the calculated $^3T_{1g} - {}^1E_g$, $^1T_{2g}$ absorption band. The wide absorption band at about 37000 cm^{-1} in the experimental spectrum was assigned to the charge transfer transition [3] (not calculated in this work).

Its intensity is nearly 10^4 times lower than the intensities of the spin-allowed transitions. The position of the calculated $^3T_{1g} - {}^1E_g$, $^1T_{2g}$ absorption band is shifted to lower energies compared with experimental results (see also Table 1). One possible reason is that this is a spin-forbidden transition and the correlation effects are different for the states with different multiplicity. This point requires a further investigation.

Comparing the results of our calculations with previous theoretical works [5, 6], we can say that the overestimation of the calculated energy levels is also seen in [5, 6] (Table 1, columns 3 – 6). The calculations of the energy levels carried out in [6] for two different distances between the chromium and fluorine ions have shown a clear (and quite expected) trend: The overestimation of the observed energy levels goes down when increasing the interionic separation. This led the author of [6] to the conclusion that the actual distance between Cr^{4+} and F^- should be greater than 1.72 Å. This point of view seems to be not correct. We have used in our calculations the actual $Cr^{4+} - F^-$ distance 1.72 Å reported in [10, 11]. Though we also got an overestimation of the calculated energy levels, the calculations of the spectral band shapes and their relative intensities follow the experimental results quite closely (the absorption spectrum was not calculated in [6]). Therefore we believe that the deviation of the $Cr^{4+} - F^-$ distance

Table 2. Partial contributions (in %) of atomic 3d-orbitals from Cr^{4+} and 2p- and 2s-orbitals from F^- to the 3d-MO's in the octahedral $[CrF_6]^{2-}$ cluster.

	Cr^{4+} 3d-orbitals	F^- 2p-orbitals	F^- 2s-orbitals
t_{2g} levels	85.39	14.60	0.00
	85.40	14.60	0.00
	85.44	14.56	0.00
e_g levels	74.76	24.07	1.17
	74.73	24.09	1.18
Averaged	81.15	18.38	0.47

from the literature data in the Rb_2CrF_6 crystal is very unlikely.

Table 2 contains the results of the Mulliken's population analysis [27]. The averaged contributions of the chromium 3d-orbitals, fluorine 2p- and 2s-orbitals into the 3d-MO are shown. As seen from the table, the averaged contribution of the 2p-orbitals is about 18.38%, and that one of the 2s-orbital is about 0.5%. Since the d – d transitions are parity-forbidden, the contributions from the states of opposite than 3d parity result in non-zeroth values of the transition intensities and make the d – d transitions possible.

The contribution of the fluorine's 2p- and 2s-orbitals to the 3d-MO follows geometric properties of the considered impurity center. In the octahedral cluster the t_{2g} orbitals are directed from the central ion into the space between the ligands, whereas the e_g orbitals are directed toward the ligands. Therefore, the contribution of the ligand's 2p- and 2s-states should be greater in the case of the e_g orbitals, as confirmed by data in Table 2.

5. Conclusion

First-principles analysis of the optical spectra of octahedrally coordinated Cr^{4+} in Rb_2CrF_6 was performed in the present paper. The energies of the Cr^{4+} multiplets were computed; their values agree well with the experimental results on the ground state absorption measurements reported in [3], if the scaling factor 0.7169 is taken into account. The absorption spectrum was modeled; the calculated positions of the absorption bands follow the measured ones. Since contribution of the ligands wave functions into the Cr^{4+} ion 3d-MO can be thought of as a measure of covalency of the chemical bond formed between the central ion and ligands, it was possible to estimate the covalency effects by performing the numerical analysis of the MO populations. The contributions of the atomic chromium 3d-orbitals, fluorine 2s- and 2p-orbitals to the MO 3d-orbital were determined. It was shown that the average contribution of the fluorine 2p-orbitals is about 18.4%, and the averaged contribution of the fluorine 2s-orbitals is about 0.5%. Such a not negligible mixture reveals a high degree of covalency in the considered crystal.

Acknowledgements

Fruitful discussions with Associate Professor K. Ogasawara (Kwansei Gakuin University) and members of the Computational Materials Science Unit at Kyoto University are gratefully acknowledged.

[1] S. Kück, Appl. Phys. B **72**, 515 (2001).
[2] I. T. Sorokina, Topics Appl. Phys. **89**, 255 (2003).
[3] G. C. Allen and G. A. M. El-Sharkawy, Inorg. Nucl. Chem. Lett. **6**, 493 (1970).
[4] S. Gutierrez Orellana and L. Pueyo, J. Sol. State Chem. **55**, 30 (1984).
[5] K. Pierloot, E. Van Praet, and L. G. Vanquickenborne, J. Chem. Phys. **102**, 1164 (1995).
[6] J. L. Pascual, J. Chem. Phys. **109**, 11129 (1998).
[7] Z. Barandiarán and L. Seijo, J. Chem. Phys. **89**, 5739 (1988).
[8] Z. Barandiarán and L. Seijo, in: Studies in Physical and Theoretical Chemistry, Vol. 77(B), Computational Chemistry: Structure, Interactions and Reactivity (Ed. S. Fraga), Elsevier, Amsterdam 1992, p. 435.
[9] K. Ogasawara, T. Iwata, Y. Koyama, T. Ishii, I. Tanaka, and H. Adachi, Phys. Rev. B **64**, 115413 (2001).
[10] H. Bode and E. Voss, Z. Anorg. Allg. Chem. **286**, 136 (1956).
[11] P. E. Tomaszewski, Phase Transitions **38**, 127 (1992).
[12] S. Watanabe and H. Kamimura, Mater. Sci. Eng. B **3**, 313 (1989).
[13] T. Ishii, K. Ogasawara, H. Adachi, and I. Tanaka, J. Chem. Phys. **115**, 492 (2001).
[14] T. Ishii, K. Fujimura, K. Ogasawara, H. Adachi, and I. Tanaka, J. Phys.: Condens. Matter **13**, 5757 (2001).
[15] M. G. Brik, T. Ishii, A. M. Tkachuk, S. E. Ivanova, and I. K. Razumova, J. Alloys Compd. **374**, 63 (2004).
[16] T. Ishii, K. Fujimura, K. Sato, M. G. Brik, and K. Ogasawara, J. Alloys Compd. **374**, 18 (2004).
[17] K. Ogasawara, S. Watanabe, H. Toyoshima, T. Ishii, M. G. Brik, H. Ikeno, and I. Tanaka, J. Sol. State Chem. **178**, 412 (2005).
[18] K. Ogasawara, S. Watanabe, Y. Sakai, H. Toyoshima, T. Ishii, M. G. Brik, and I. Tanaka, Jpn. J. Appl. Phys. **43**, L611 (2004).
[19] K. Ogasawara, S. Watanabe, T. Ishii, and M. G. Brik, Jpn. J. Appl. Phys. **44**, 7488 (2005).

[20] K. Ogasawara, T. Miyamae, I. Tanaka, and H. Adachi, Mater. Trans. **43**, 1435 (2002).
[21] H. Ikeno, I. Tanaka, L. Miyamae, T. Mishima, H. Adachi, and K. Ogasawara, Mater. Trans. **45**, 1414 (2004).
[22] H. Ikeno, I. Tanaka, Y. Koyama, T. Mizoguchi, and K.Ogasawara, Phys. Rev. B **72**, 075123 (2005).
[23] S. Sugano, Y. Tanabe, and H. Kamimura, Multiplets of Transition-Metal Ions in Crystals, Academic Press, New York 1970.
[24] M. G. Brik, N. M. Avram, C. N. Avram, and I. Tanaka, Eur. Phys. J. Appl. Phys. **29**, 239 (2005).
[25] P. Kubelka and F. Munk, Z. Tech. Phys. **12**, 593 (1931).
[26] P. Kubelka, J. Opt. Soc. Am. **98**, 448 (1948).
[27] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).