The Determination of Molecular Quantities from Measurements on Macroscopic Systems

III. Electro-optical Absorption Measurements on Michler's Ketone

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Some bulk quantities appropriate for the description of electro-optical absorption measurements on macroscopic systems are defined and their properties are discussed. Based on three molecular models (Lorentz model, Onsager model in spherical approximation and in ellipsoidal approximation) model molar quantities are introduced, which depend on intrinsic properties of the molecule (dipole moments and polarizabilities in the ground and excited state, transition dipole moment and transition polarizability). The relations will be applied for the evaluation of the results of electro-optical absorption measurements on Michler's ketone in cyclohexane in a wavenumber interval near $30 \cdot 10^5$ m^{-1}. The angles between the dipole moments in the ground and the excited state and the transition dipole moment will be determined; the magnitude of the dipole moment in the corresponding excited state is $\mu_{aG} = 30 \cdot 10^{-30}$ Cm. The data show that the symmetry of a solute Michler's ketone molecule most probably corresponds, at least approximately, to the point group C_s.

1. Introduction

For a macroscopic phase meeting a few general requirements [1], it is possible to define certain bulk quantities without introducing any assumption relating to the particular molecular structure of the considered phase. Of special interest are extensive quantities and their adjoint densities, as defined by (I.21)*, since original experimental quantities directly determined with suitable measurement devices, belong mostly either to one or the other type or can easily be transformed into one. These quantities usually depend on the composition of the phase. Knowledge of their values for varying composition allows the determination of corresponding partial molar quantities (PMQ's) defined by (I.22). The PMQ's are also describing bulk properties independent of any molecular model. To relate the PMQ's to molecular quantities necessitates the introduction of an appropriate molecular model allowing the definition of corresponding model molar quantities (MMQ's). Some general relations between PMQ's and MMQ's pertinent to electro-optical absorption measurements have been presented in paper I of this series [1]. In this paper the relations between the MMQ's and some molecular quantities are outlined, based on a separate molecular model (SMM) described previously [1]. The relations are used to determine properties of isolated molecules from electro-optical absorption measurements on solutions, as will be exemplified for Michler's ketone.

2. The Model for the Evaluation of Electro-optical Absorption Measurements

With suitable devices for electro-optical absorption measurements [3, 4] a quantity M can be determined, which has been defined by (I.166),

$$M = \lim_{E_a^2 \to 0} (\partial a_E / \partial E_a^2)_{n_{0I}, \vartheta_i'}, \quad (1)$$

where a_E is the absorption coefficient of the phase in the presence of an applied uniform electric field with magnitude E_a. The quantity M describes a bulk property and for phases which are isotropic in the absence of an applied field, M is necessarily independent of E_a. From the values of M, measured at varying compositions of the phase, the value of the PMQ Υ_{0G}, as defined by (I.167), can be determined and for phases meeting a few requirements also the value of the corresponding MMQ v_G, as was outlined in Sect. 9.5 of paper I of this series [1].

For the determination of molecular quantities of some particular molecule by the electro-optical absorption of solutions, one usually chooses a pure

* The abbreviations Eq. (I....) or Eq. (II....) denote equations of paper I [1] or II [2] of this series, respectively.

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solvent (substance A_1) with negligible optical absorption in the absorption ranges of interest of the solute (substance A_G). Under this circumstance (I.175) nearly always holds true and hence also

$$v_G^* = (M/c_{0G})^*, \tag{2}$$

where c_{0G} is the initial concentration of the solute A_G. Any quantity with a star as a superscript is the limit of the quantity for the pure solvent as defined by (I.37). The limit v_G^* of the MMQ v_G is related to molecular quantities by an equation similar to (I.170)

$$v_G^* = \varkappa_G^*(L_G^* + q_G^* + s_E^*), \tag{3}$$

where

$$L_G^* = \lim_{E_a^2 \to 0} \frac{1}{\varkappa_{EG}^*} \left(\frac{\partial \varkappa_{EG}^*}{\partial E_a^2}\right)_{n_{0I}, \vartheta_{i'}} \tag{4}$$

describes the relative change of the molar absorption coefficient $\varkappa_{EG}^*$ caused by the applied electric field. The quantities q_G^* and s_E^* are the limits of q_G and s_E as defined by (I.172) and (I.173), respectively. The quantity q_G represents the relative change of the mole ratio r_{EG} of the solute A_G due to an applied field and s_E the effects caused by the electrostriction of the solution.

In sufficiently dilute solutions at wavenumber intervals where the solvent does not absorb, the absorption coefficient a is usually proportional to the concentration c_{0G} of the solute, i.e. $a = \varkappa_G^* c_{0G}$, where $\varkappa_G^*$ is the molar absorption coefficient of A_G. Similarly, under the same conditions it is according to (I.175) $M = v_G^* c_{0G}$, such that

$$L_G^* + q_G^* + s_E^* = \frac{v_G^*}{\varkappa_G^*} = \frac{M}{a} = \frac{\mathsf{Y}_{0G}^*}{\mathsf{K}_{0G}^*}, \tag{5}$$

where K_{0G}^* is the limit of the partial molar absorption of the solute A_G as defined by (I.160). In a solution without any chemical reaction the quantities q_G^* and s_E^* are usually assumed negligibly small compared to L_G^*. In this case the quantity L_G^* can be obtained from the measured quantities M and a, even if the concentration of the solute A_G is unknown.

The quantity L_G^* depends on intrinsic properties of the molecule A_G which we wish to determine, on properties of the solvent, assumed to be representable as functions of the relative permittivity ε_r^* and the square of the refractive index n^{*2} of the solvent, on the temperature T and on properties of the light used. These are the wavenumber $\tilde{\nu}$ and, using linearly polarized light, the angle χ between the polarization direction and the direction of the applied uniform electric field. The molecular model extensively treated previously [3, 5], applies to the case when a wavenumber interval corresponding to an isolated absorption band is investigated and produces the following result*:

$$\begin{aligned} L_G^*(\tilde{\nu}, \chi) = {} & D_G^* r(\chi) + (E_G^*/6)\, s(\chi) \\ & + F_G^* r(\chi)\, t_G^*(\tilde{\nu}) + G_G^* s(\chi)\, t_G^*(\tilde{\nu}) \\ & + H_G^* r(\chi)\, u_G^*(\tilde{\nu}) + I_G^* s(\chi)\, u_G^*(\tilde{\nu}), \end{aligned} \tag{6}$$

where

$$r(\chi) = (2 - \cos^2 \chi)/5, \tag{7}$$

$$s(\chi) = (3 \cos^2 \chi - 1)/5, \tag{8}$$

$$\begin{aligned} t_G^*(\tilde{\nu}) &= \frac{\tilde{\nu}}{h c \varkappa_G^*} \left(\frac{\partial \varkappa_G^*/\tilde{\nu}'}{\partial \tilde{\nu}'}\right)_{\tilde{\nu}'=\tilde{\nu}} \\ &= \frac{1}{h c} \left(\frac{\partial \ln(\varkappa_G^*/\tilde{\nu}')}{\partial \tilde{\nu}'}\right)_{\tilde{\nu}'=\tilde{\nu}}, \end{aligned} \tag{9}$$

and

$$u_G^*(\tilde{\nu}) = \frac{\tilde{\nu}}{2 h^2 c^2 \varkappa_G^*} \left(\frac{\partial^2 \varkappa_G^*/\tilde{\nu}'}{\partial \tilde{\nu}'^2}\right)_{\tilde{\nu}'=\tilde{\nu}} \tag{10}$$

$$= \frac{1}{2 h^2 c^2} \left[\left(\frac{\partial \ln(\varkappa_G^*/\tilde{\nu}')}{\partial \tilde{\nu}'}\right)_{\tilde{\nu}'=\tilde{\nu}} + \left(\frac{\partial^2 \ln(\varkappa_G^*/\tilde{\nu}')}{\partial \tilde{\nu}'^2}\right)_{\tilde{\nu}'=\tilde{\nu}}\right].$$

The quantities $r(\chi)$ and $s(\chi)$ are determined by the chosen angle between the direction of the applied uniform electric field $\boldsymbol{E}_a$ and the direction of the electric field vector of the incident light, which is used for the electro-optical absorption measurements. The quantities $t_G^*(\tilde{\nu})$ and $u_G^*(\tilde{\nu})$ can be estimated from the shape of the absorption band of the investigated molecule in the absence of an applied field in the same solvent as used for the electro-optical absorption measurements. A set of data $L_G^*(\tilde{\nu}, \chi)$ for various values of $r(\chi)$, $s(\chi)$, $r(\chi)\, t_G^*(\tilde{\nu})$, $s(\chi)\, t_G^*(\tilde{\nu})$, $r(\chi)\, u_G^*(\tilde{\nu})$ and $s(\chi)\, u_G^*(\tilde{\nu})$ can be evaluated by multiple regression leading to estimators for the quantities D_G^*, E_G^*, F_G^*, G_G^*, H_G^*, and I_G^* and for their standard deviations. These quantities are connected to intrinsic molecular properties as can be recognized from the following equations (where

* Some of the symbols are differently defined in previous papers, i.e. $E = E$ (previous) $+ 2D$, $3G = G$ (previous) $+ F$, $3I = I$ (previous) $+ H$.

the superscript star and the subscript G are omitted for simplification):

$$D = \frac{1}{kT}\tilde{\boldsymbol{R}}^{(1)}\,\mathbf{f}_e^2\,\boldsymbol{\mu} + f_e^2 S^{(1)}, \tag{11}$$

$$E = \frac{1}{k^2T^2}\left[3(\tilde{\boldsymbol{m}}\,\mathbf{f}_e\,\boldsymbol{\mu})^2 - \tilde{\boldsymbol{\mu}}\,\mathbf{f}_e^2\,\boldsymbol{\mu}\right] + \frac{1}{kT}\left[3\,\tilde{\boldsymbol{m}}\,\mathbf{f}_e^2\,\boldsymbol{\alpha}\,\boldsymbol{m} - \mathrm{tr}\,(\mathbf{f}_e^2\,\boldsymbol{\alpha})\right] + \frac{3}{kT}\tilde{\boldsymbol{R}}^{(2)}\,\mathbf{f}_e^2\,\boldsymbol{\mu} + 3f_e^2 S^{(2)} + Q^{(1)}(\boldsymbol{E}_f), \tag{12}$$

$$F = (1/kT)\,\tilde{\boldsymbol{\mu}}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\mu} + \tfrac{1}{2}\,\mathrm{tr}\,(\mathbf{f}_e^2\,\Delta\boldsymbol{\alpha}) + \tilde{\boldsymbol{R}}^{(1)}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\mu} + Q^{(2)}(\boldsymbol{E}_f), \tag{13}$$

$$G = (1/kT)\,(\tilde{\boldsymbol{m}}\,\mathbf{f}_e\,\boldsymbol{\mu})\,(\tilde{\boldsymbol{m}}\,\mathbf{f}_e\,\Delta\boldsymbol{\mu}) + \tfrac{1}{2}\,\tilde{\boldsymbol{m}}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\alpha}\,\boldsymbol{m} + \tfrac{1}{2}\,\tilde{\boldsymbol{R}}^{(2)}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\mu} + Q^{(3)}(\boldsymbol{E}_f), \tag{14}$$

$$H = \Delta\tilde{\boldsymbol{\mu}}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\mu} + Q^{(4)}(\boldsymbol{E}_f), \tag{15}$$

$$I = (\tilde{\boldsymbol{m}}\,\mathbf{f}_e\,\Delta\boldsymbol{\mu})^2 + Q^{(5)}(\boldsymbol{E}_f), \tag{16}$$

where

$$\boldsymbol{\mu} = (\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_g)^{-1}\,\boldsymbol{\mu}_g, \tag{17}$$

$$\Delta\boldsymbol{\mu} = (\mathbf{1} - \mathbf{f}'\,\boldsymbol{\alpha}_a)^{-1}(\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_g)^{-1} \cdot (\mathbf{1} - \mathbf{f}'\,\boldsymbol{\alpha}_g)\,(\boldsymbol{\mu}_a - \boldsymbol{\mu}_g) + \mathbf{f}\,\Delta\boldsymbol{\alpha}\,\boldsymbol{\mu}_g, \tag{18}$$

$$\boldsymbol{\alpha} = (\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_g)^{-1}\,\boldsymbol{\alpha}_g, \tag{19}$$

$$\Delta\boldsymbol{\alpha} = (\mathbf{1} - \mathbf{f}'\,\boldsymbol{\alpha}_a)^{-1}(\mathbf{1} - \mathbf{f}\,\boldsymbol{\alpha}_g)^{-2} \cdot (\mathbf{1} - \mathbf{f}'\,\boldsymbol{\alpha}_g)\,(\boldsymbol{\alpha}_a - \boldsymbol{\alpha}_g). \tag{20}$$

$\boldsymbol{\mu}_g = \boldsymbol{\mu}_{gG}$, $\boldsymbol{\mu}_a = \boldsymbol{\mu}_{aG}$, $\boldsymbol{\alpha}_g = \boldsymbol{\alpha}_{gG}$ and $\boldsymbol{\alpha}_a = \boldsymbol{\alpha}_{aG}$ are the permanent electric dipole moments and static electric polarizabilities in the ground state and the considered Franck-Condon excited vibronic (electronic vibrational) state, respectively, of the isolated molecule A_G. $\boldsymbol{m} = \boldsymbol{m}_G^*$ is a unit vector in direction of the transition dipole moment $\boldsymbol{\mu}_{gaG}^*$ of the considered vibronic excitation. T is the temperature and k the Boltzmann constant. The tensors $\mathbf{f}_e = \mathbf{f}_{eG}^*$, $\mathbf{f} = \mathbf{f}_G^*$ and $\mathbf{f}' = \mathbf{f}_G'^*$ describe the dependences on properties of the solvent in the model used for the representation of the MMQ. They are dependent on ε_r^* and n^{*2}, the formulas being given by (II.32) to (II.37). In the derivation of the above equations it was assumed that all tensor products are commutative which is necessarily true if all tensors own identical principal axes.

The quantities $\boldsymbol{\mu}$, $\Delta\boldsymbol{\mu}$, $\boldsymbol{\alpha}$ and $\Delta\boldsymbol{\alpha}$ are roughly the dipole moment and the polarizability and the changes of those quantities during the excitation process of the molecule A_G in the solution. To obtain the corresponding intrinsic quantities of the isolated molecule, Eqs. (17) to (22) have to be applied. The vectors $\boldsymbol{R}^{(1)} = \boldsymbol{R}_G^{(1)*}$ and $\boldsymbol{R}^{(2)} = \boldsymbol{R}_G^{(2)*}$ and the scalars $S^{(1)} = S_G^{(1)*}$ and $S^{(2)} = S_G^{(2)*}$ are related to the transition polarizability $\boldsymbol{\alpha}_{gaG}^*$ [6]. For many molecules the term D_G^*, caused by the field dependence of the transition moment, is relatively small compared to E_G^* and then commonly it is assumed that the terms dependent on $\boldsymbol{R}^{(2)}$ as well as on $\boldsymbol{R}^{(1)}$ can be neglected. The terms dependent on $S^{(1)}$ and $S^{(2)}$ are usually an order of magnitude smaller than those dependent on $\boldsymbol{R}^{(1)}$ and $\boldsymbol{R}^{(2)}$ and hence can also be neglected. The quantities $Q^{(i)}(\boldsymbol{E}_f)$, $i = 1, \ldots, 5$, represent the contributions to $E, \ldots, I$, respectively, caused by the fluctuation $\boldsymbol{E}_f$ of the electric field [2, 5, 7]. In suitable solvents as in aliphatic hydrocarbons, for example (but not in benzene or dioxane, where the solvent molecules own relatively large quadrupole moments [8]), the average $\langle\tilde{\boldsymbol{E}}_f\,\boldsymbol{E}_f\rangle$ is vanishingly small and the terms $Q^{(i)}(\boldsymbol{E}_f)$ in (12) to (16) can be neglected.

For a molecule with a sufficiently large magnitude of the dipole moment $\boldsymbol{\mu}_{gG}$, the second term on the right-hand side of (12) dependent on $\boldsymbol{\alpha}_{gG}$ is usually small compared to the first term. In this case the second term can be estimated or even neglected without introducing an appreciable error. Usually it is furthermore assumed that all terms dependent on the change of the polarizability $(\boldsymbol{\alpha}_{ag} - \boldsymbol{\alpha}_{gG})$ are also negligibly small. If all quantities E_G^* to I_G^* can be determined from experimental data with sufficiently small errors, then with the above neglects it is possible to determine the magnitudes of $\boldsymbol{\mu}$ and $\Delta\boldsymbol{\mu}$ and the angles $\sphericalangle(\boldsymbol{m}, \boldsymbol{\mu})$, $\sphericalangle(\boldsymbol{m}, \Delta\boldsymbol{\mu})$ and $\sphericalangle(\boldsymbol{\mu}, \Delta\boldsymbol{\mu})$ between these vectors and the direction $\boldsymbol{m} = \boldsymbol{m}_G^*$ of the transition dipole moment $\boldsymbol{\mu}_{gaG}^*$ of the solute molecule A_G. From such data some assertions about the structure of the molecule in its ground state in solution can be gained in favorable cases, as will be shown in Sect. 3 and also in the fifth paper of this series [9]. Furthermore the magnitudes of $\boldsymbol{\mu}_{gG}$ and $\boldsymbol{\mu}_{ag}$ and the angles $\sphericalangle(\boldsymbol{\mu}_{gG}, \boldsymbol{\mu}_{aG})$ and $\sphericalangle(\boldsymbol{m}, \boldsymbol{\mu}_{aG})$ can be determined.

The derivations of (11) to (20) are based on the extended Onsager model in ellipsoidal approximation. In spherical approximation the same equations result but with the tensors $\mathbf{f}_e$, $\mathbf{f}$ and $\mathbf{f}'$ replaced by the corresponding scalars. If the derivation is based

on the Lorentz model, the resulting equations are similar, but in (11) to (20) $\boldsymbol{\mu}$ has to be replaced by $\boldsymbol{\mu}_{gG}$, $\Delta\boldsymbol{\mu}$ by $\boldsymbol{\mu}_{aG} - \boldsymbol{\mu}_{gG}$, $\boldsymbol{\alpha}$ by $\boldsymbol{\alpha}_{gG}$, $\Delta\boldsymbol{\alpha}$ by $\boldsymbol{\alpha}_{aG} - \boldsymbol{\alpha}_{gG}$, $\mathbf{f}_e$ by $f_{\text{Lorentz}} = (\varepsilon_r + 2)/3$ and the terms depending on $\boldsymbol{E}_f$ have to be cancelled. To compare the models, the following evaluation will be performed for all three of them.

3. The Determination of Macroscopic and Molecular Quantities

3.1. The Investigated System and the Measuring Devices

Solutions of 4,4'-(bis-dimethylamino)-benzophenone (Michler's ketone) in cyclohexane were investigated in the wavenumber interval $\tilde{\nu} = 28$ to $31 \cdot 10^5\ \text{m}^{-1}$ at concentrations of approximately $c_{0G} = 0.02\ \text{mol m}^{-3}$ and temperature 298.1 K. Measurements of the fluorescence have shown that in this range the degree of anisotropy R_f is nearly 0.4 [10], even in liquid solutions in ethanol. Therefore in that range the molecule owns a unique direction $\boldsymbol{m}$ of the transition dipole moment, and hence the prerequisite for the validity of (5) with (7) to (16) is met. The relative changes of the molar absorption coefficients in an applied electric field have been measured with a device introduced by Labhart [3, 4, 11], and the molar absorption coefficients with a spectralphotometer Zeiss PMQ II 2 supplied with a double monochromator MM 12.

3.2. Evaluation, Results and Discussion

In Table 1 the data of optical absorption measurements and electrooptical absorption measurements are represented. The values of $L_G^*(\tilde{\nu}, \chi)$ are averages of six measurements. A multiple regression according to (6) leads to estimators for the quantities D_G^* to I_G^* as reported in Table 2. The errors given are 95% confidence limits based on the Student's t-distribution ($\pm t_{1-\alpha} s$, where s is the standard deviation of the mean and $\alpha = 0.025$). With the estimators of D_G^* to I_G^* the values of L_G^* are calculated using (6) and the experimentally determined values of r, s, t and u. The differences

$$\Delta L_G^* = (L_G^*)_{\text{determined}} - (L_G^*)_{\text{calculated}},$$

which are also listed in Table 1, are smaller or comparable to expected experimental errors and do not show any significant trend with the wavenumber $\tilde{\nu}$. Therefore the quantities L_G^* satisfy (6) within experimental errors and this fact confirms the assumption that the considered wavenumber interval corresponds to an isolated absorption band [3, 5] as was expected from the degree of anisotropy of the fluorescence [10]. Furthermore, possible contributions caused by a weak long-wave band [12, 13] are negligible in that range [$(28.7$ to $30.3) \cdot 10^5\ \text{m}^{-1}$].

The further evaluation is based on (11) to (16). In the solvent cyclohexane it is $\langle \tilde{\boldsymbol{E}}_f \boldsymbol{E}_f \rangle \approx 0$ [8], and hence the terms $Q^{(1)}(\boldsymbol{E}_f)$ can be neglected. The

Table 1. Absorption coefficients $\varkappa_G^*(\tilde{\nu})$ and quantities $L_G^*(\tilde{\nu}, \chi)$ of Michler's ketone in cyclohexane ($T = 298.1$ K).

		$\chi = 0°$		$\chi = 54.7°$		$\chi = 90°$	
$\tilde{\nu}$	$\varkappa_G^*$	L_G^*	ΔL_G^*	L_G^*	ΔL_G^*	L_G^*	ΔL_G^*
$10^4\ \text{m}^{-1}$	$\text{m}^2\ \text{mol}^{-1}$	$10^{-19}\ \text{V}^{-2}\ \text{m}^2$	$10^{-19}\ \text{V}^{-2}\ \text{m}^2$	$10^{-19}\ \text{V}^{-2}\ \text{m}^2$	$10^{-19}\ \text{V}^{-2}\ \text{m}^2$	$10^{-19}\ \text{V}^{-2}\ \text{m}^2$	$10^{-19}\ \text{V}^{-2}\ \text{m}^2$
287	1593	22.58	− 0.17	27.86	0.03	30.04	− 0.33
288	1865	19.41	0.06	25.17	0.20	27.84	0.06
289	2146	15.55	− 0.44	22.30	0.19	25.22	0.04
290	2437	12.41	− 0.07	19.52	0.44	22.53	0.14
291	2718	8.96	− 0.33	16.63	0.31	19.76	− 0.07
292	3003	6.04	0.06	13.80	0.40	17.18	0.08
293	3278	2.92	0.03	10.97	0.33	14.63	0.11
294	3509	0.16	0	8.39	0.20	12.09	− 0.12
295	3698	− 2.36	0.01	5.97	0.08	9.68	− 0.35
296	3888	− 4.89	− 0.19	3.73	0	7.55	− 0.41
297	3983	− 6.82	0.07	1.60	− 0.12	5.75	− 0.27
298	4078	− 8.79	0	0.027	0.10	4.16	− 0.11
299	4106	− 10.05	0.25	− 1.43	0.12	2.76	− 0.06
300	4093	− 11.60	− 0.04	− 2.71	0.10	1.63	0.06
301	4046	− 12.26	0.16	− 3.52	0.20	0.81	0.18
302	3951	− 12.80	0.03	− 4.08	0.16	0.14	0.06
303	3872	− 13.28	− 0.19	− 4.53	0.04	− 0.42	− 0.11

Table 2. Estimators for the quantities D_G^* to I_G^*.

$D_G^*/10^{-19}\ \mathrm{V^{-2}\,m^2}$	2 ± 4
$E_G^*/10^{-19}\ \mathrm{V^{-2}\,m^2}$	-117 ± 4
$F_G^*/10^{-40}\ \mathrm{CV^{-1}\,m^2}$	965 ± 11
$G_G^*/10^{-40}\ \mathrm{CV^{-1}\,m^2}$	381 ± 7
$H_G^*/10^{-60}\ \mathrm{C^2\,m^2}$	460 ± 40
$I_G^*/10^{-60}\ \mathrm{C^2\,m^2}$	310 ± 60

quantity D_G^* is small compared to the magnitude of E_G^*, and therefore it may be assumed that all terms describing the field dependence of the transition dipole moment ($\boldsymbol{R}^{(1)}$, $\boldsymbol{R}^{(2)}$, $S^{(1)}$, $S^{(2)}$) can be neglected. The term $3\,\tilde{\boldsymbol{m}}\,\mathbf{f}_e^2\,\boldsymbol{\alpha}\,\boldsymbol{m} - \mathrm{tr}\,(\mathbf{f}_e^2\,\boldsymbol{\alpha})$ can be estimated using the data listed in Table 2 of paper II of this series [2], and produces the value

$$(kT)^{-1}[3\,\tilde{\boldsymbol{m}}\,\mathbf{f}_e^2\,\boldsymbol{\alpha}\,\boldsymbol{m} - \mathrm{tr}\,(\mathbf{f}_e^2\,\boldsymbol{\alpha})] = -(12 \pm 5)\cdot 10^{-19}\ \mathrm{V^{-2}\,m^2}\,.$$

Since this term is small compared to E_G^*, even some inaccuracy would not affect the further evaluations. Neglecting furthermore the changes of the polarizability ($\Delta\boldsymbol{\alpha} \approx 0$), the following quantities can be estimated (where again the superscript star and the subscript G are omitted for simplification):

$$(\tilde{\boldsymbol{m}}\,\mathbf{f}_e\,\boldsymbol{\mu})^2 = k^2T^2\frac{G^2}{I} = (80 \pm 15)\cdot 10^{-60}\ \mathrm{C^2\,m^2}\,, \tag{21}$$

$$(\tilde{\boldsymbol{m}}\,\mathbf{f}_e\,\Delta\boldsymbol{\mu})^2 = I = (300 \pm 60)\cdot 10^{-60}\ \mathrm{C^2\,m^2}\,, \tag{22}$$

$$\tilde{\boldsymbol{\mu}}\,\mathbf{f}_e^2\,\boldsymbol{\mu} = k^2T^2\left\{\frac{3G^2}{I} - E + \frac{1}{kT}[3\,\tilde{\boldsymbol{m}}\,\mathbf{f}_e^2\,\boldsymbol{\alpha}\,\boldsymbol{m} - \mathrm{tr}\,(\mathbf{f}_e^2\,\boldsymbol{\alpha})]\right\} = (420 \pm 40)\cdot 10^{-60}\ \mathrm{C^2\,m^2}\,, \tag{23}$$

$$\Delta\tilde{\boldsymbol{\mu}}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\mu} = H = (460 \pm 40)\cdot 10^{-60}\ \mathrm{C^2\,m^2}\,, \tag{24}$$

$$\tilde{\boldsymbol{\mu}}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\mu} = kTF = (397 \pm 4)\cdot 10^{-60}\ \mathrm{C^2\,m^2}. \tag{25}$$

The above and further quantities have been estimated individually for each set of measurements; the data reported are averages of individual results. For the angle $\sphericalangle(\boldsymbol{m}, \mathbf{f}_e\boldsymbol{\mu})$ between the unit vector $\boldsymbol{m}$ in direction of the transition moment and the vector $\mathbf{f}_e\boldsymbol{\mu}$ any two values ϑ and $\pi - \vartheta$ are equivalent because for a transition moment vector only its orientation can be determined but not its direction (a transition moment vector and the opposite vector cannot be distinguished). Therefore the interval for this angle is $0 \leqq \sphericalangle(\boldsymbol{m}, \mathbf{f}_e\boldsymbol{\mu}) < \pi/2$. Since $G > 0$, from (14) follows that the value of the angle between the vectors $\boldsymbol{m}$ and $\mathbf{f}_e\Delta\boldsymbol{\mu}$ is also restricted to

$$0 \leqq \sphericalangle(\boldsymbol{m}, \mathbf{f}_e\Delta\boldsymbol{\mu}) < \pi/2\,,$$

and similarly since $F > 0$, from (13) follows

$$0 \leqq \sphericalangle(\mathbf{f}_e\boldsymbol{\mu}, \mathbf{f}_e\Delta\boldsymbol{\mu}) < \pi/2\,.$$

Hence these three angles are uniquely determined:

$$\sphericalangle(\boldsymbol{m}, \mathbf{f}_e\boldsymbol{\mu}) = \cos^{-1}\left\{\frac{|\tilde{\boldsymbol{m}}\,\mathbf{f}_e\boldsymbol{\mu}|}{\|\mathbf{f}_e\boldsymbol{\mu}\|}\right\} = 64^\circ \pm 1^\circ\,,$$

$$\sphericalangle(\boldsymbol{m}, \mathbf{f}_e\Delta\boldsymbol{\mu}) = \cos^{-1}\left\{\frac{|\tilde{\boldsymbol{m}}\,\mathbf{f}_e\Delta\boldsymbol{\mu}|}{\|\mathbf{f}_e\Delta\boldsymbol{\mu}\|}\right\} = 36^\circ \pm 5^\circ\,,$$

$$\sphericalangle(\mathbf{f}_e\boldsymbol{\mu}, \mathbf{f}_e\Delta\boldsymbol{\mu}) = \cos^{-1}\left\{\frac{\tilde{\boldsymbol{\mu}}\,\mathbf{f}_e^2\,\Delta\boldsymbol{\mu}}{\|\mathbf{f}_e\boldsymbol{\mu}\|\cdot\|\mathbf{f}_e\Delta\boldsymbol{\mu}\|}\right\} = 26^\circ \pm 4^\circ\,.$$

The angle ψ between the planes spanned by the vectors $\boldsymbol{m}$ and $\mathbf{f}_e\boldsymbol{\mu}$ and the vectors $\mathbf{f}_e\boldsymbol{\mu}$ and $\mathbf{f}_e\Delta\boldsymbol{\mu}$ is according to the above data: $\psi = 0^\circ \pm 30^\circ$.

One has to expect that the symmetry of Michler's ketone belongs to one of the following point groups:

C_{2v}: Both phenyl groups coplanar or perpendicular to the plane of the C-CO-C group.

C_2: Both phenyl groups twisted by the same angle out of the C-CO-C plane (propeller shape).

C_s: One of the phenyl groups coplanar to the plane of the C-CO-C group, the plane of the other phenyl group perpendicular to the C-CO-C plane.

C_1: Without any particular symmetry property.

The point group C_2 was found in crystals of p,p'-dimethoxybenzophenone [14], and based on that point group data of NMR measurements of Michler's ketone have been explained [15]. The point group C_s was discussed by Higasi and Smyth [16] for derivatives of benzophenone, and from data of dipole moment measurements the group C_s for Michler's ketone was assumed by Feichtmayr, Schlag and Würstlin [17].

In case of C_{2v} or C_2 it has to be $\sphericalangle(\boldsymbol{m}, \mathbf{f}_e\boldsymbol{\mu}) = 0^\circ$ or 90°, $\sphericalangle(\boldsymbol{m}, \mathbf{f}_e\Delta\boldsymbol{\mu}) = 0^\circ$, 90° or 180° and $\sphericalangle(\mathbf{f}_e\boldsymbol{\mu}, \mathbf{f}_e\Delta\boldsymbol{\mu}) = 0^\circ$ or 180°. The above data are in contradiction to these requirements, and hence any molecular models with C_{2v} or C_2 symmetry are falsified. This conclusion follows also from the val-

ues of H_G^* and I_G^*, because in case of C_{2v} or C_2 according to (15) and (16) it has to be either $I_G^* = 0$ or $I_G^* = H_G^*$, which disagrees with the data listed in Table 2. In case of C_s, when either two of the three angles $\sphericalangle(\boldsymbol{m}, \mathbf{f}_e \boldsymbol{\mu})$, $\sphericalangle(\boldsymbol{m}, \mathbf{f}_e \Delta\boldsymbol{\mu})$ and $\sphericalangle(\mathbf{f}_e \boldsymbol{\mu}, \mathbf{f}_e \Delta\boldsymbol{\mu})$ are arbitrary, they are related by

$$\sphericalangle(\boldsymbol{m}, \mathbf{f}_e \boldsymbol{\mu}) \pm \sphericalangle(\mathbf{f}_e \boldsymbol{\mu}, \mathbf{f}_e \Delta\boldsymbol{\mu}) = \sphericalangle(\boldsymbol{m}, \mathbf{f}_e \Delta\boldsymbol{\mu})$$

such that $\psi = 0°$, or it is

$$\sphericalangle(\boldsymbol{m}, \mathbf{f}_e \boldsymbol{\mu}) = \sphericalangle(\boldsymbol{m}, \mathbf{f}_e \Delta\boldsymbol{\mu}) = 90°$$

and $\sphericalangle(\mathbf{f}_e \boldsymbol{\mu}, \mathbf{f}_e \Delta\boldsymbol{\mu})$ is arbitrary. The above data are in agreement with these requirements, and hence the assumption of the point group C_s for the symmetry of a solute Michler's ketone molecule in cyclohexane conforms with the results of electro-optical absorption measurements. The data from NMR measurements [15] are not necessarily contradictory with the assumption of the point group C_s, if a rather fast exchange of the phenyl groups coplanar and perpendicular to the C-CO-C plane occurs at $T = 298$ K [16], so that with NMR methods averages of the values of the isomers will be obtained.

The determination of the angles is independent of the particular model chosen. The further evaluation of data, i.e. the determination of $\|\boldsymbol{\mu}_{gG}\|$, $\|\boldsymbol{\mu}_{aG} - \boldsymbol{\mu}_{gG}\|$ and $\|\boldsymbol{\mu}_{aG}\|$, has to be based on a particular model. The Lorentz model as well as the Onsager model in a spherical approximation allows a straightforward evaluation, using (17) and (18) and the values of f_e, f and f', estimated as shown in paper II [2]. The Onsager model in ellipsoidal approximation can only be applied if an assumption about the direction of $\boldsymbol{\mu}_{gG}$ relative to the axes of the ellipsoid is made; we assume $\boldsymbol{\mu}_{gG}$ to be parallel to the z-axis and use the values of $\mathbf{f}_e$, $\mathbf{f}$, $\mathbf{f}'$ and $\boldsymbol{\alpha}_{gG} = \boldsymbol{\alpha}_{aG} = \mathbf{A}_{gG}$ as estimated previously [2]. The evaluation leads to the data listed in Table 3. The values of the magnitude μ_{gG} of the electric dipole moment of the ground state obtained from electro-optical absorption measurements using (23) are approximately 14% smaller than the values obtained from permittivity measurements [2], but they agree in the range of error at least if the evaluation is based on the Onsager model. This confirms the assumption that the terms depending on $\boldsymbol{R}^{(2)}$ can approximately be neglected in (12) and (14). The errors of the values of μ_{gG} obtained from electro-optical absorption measurements are equal or even smaller than those of μ_{gG} obtained from permittivity measurements. This shows that the accuracy of both methods is comparable. With both methods the accuracy is limited mainly by the imperfection of the models used for the evaluation of data or imperfect knowledge of quantities occurring in those models, but not by deficient experimental technique. The value of the magnitude μ_{aG} of the electric dipole moment in the considered electronically excited state (which is a Franck-Condon excited state [3, 5]) shows that there is a rather large increase of the dipole moment during the excitation process corresponding to the optical absorption in the wavenumber interval at $(29 \text{ to } 30) \cdot 10^5\ \text{m}^{-1}$ in cyclohexane. Therefore it seems appropriate to call the corresponding excited state an intramolecular charge-transfer state [12], but such a characterization should be used cautiously or even be avoided because there are quite similar absorption bands, where only a small change or even a decrease of the dipole moment can be observed [18]. Since solute Michler's ketone most probably has the symmetry of the point group C_s, at least approximately, and since the transition dipole moment is parallel to the symmetry plane, we prefer to call the excitation process a $\pi\pi^*$ transition between the states characterized by the electric dipole moments as given above. Based on a comparison of the absorption spectra of derivatives of benzophenone, Feichtmayr, Schlag and Würstlin [17] proposed that the one phenyl group in Michler's ketone coplanar with the C-CO-C group is the main participant in the first intense transition. This picture is supported by the values of the angles $\sphericalangle(\boldsymbol{m}, \mathbf{f}_e \boldsymbol{\mu})$ and $\sphericalangle(\boldsymbol{\mu}_{gG}, \boldsymbol{\mu}_{aG})$,

Table 3. Electric dipole moments $\boldsymbol{\mu}_{gG}$ and $\boldsymbol{\mu}_{aG}$ of Michler's ketone in the ground state and an electronically excited state (corresponding to an excitation at $\tilde{\nu} = 30 \cdot 10^5\ \text{m}^{-1}$ in cyclohexane).

	Evaluation based on		
		Onsager model	
	Lorentz model	spherical approx.	ellipsoidal approx.
From electrochromic measurements:			
$\|\boldsymbol{\mu}_{gG}\|/10^{-30}$ Cm	15.2 ± 0.7	14.1 ± 0.6	14.9 ± 0.7
$\|\boldsymbol{\mu}_{aG}\|/10^{-30}$ Cm	30.6 ± 0.3	28.3 ± 0.3	30.3 ± 0.4
$\sphericalangle(\boldsymbol{\mu}_{gG}, \boldsymbol{\mu}_{aG})$	$13° \pm 2°$	$13° \pm 2°$	$16° \pm 2°$
From permittivity measurements [2]:			
$\|\boldsymbol{\mu}_{gG}\|/10^{-30}$ Cm	17.6 ± 0.3	16.4 ± 1.2	17.1 ± 1.5

and agrees with the assignment to the point group C_s because in that conformation much of the interaction between the π electronic systems of the $CO-C_6H_4-N(CH_3)_2$ group and the perpendicular $C_6H_4-N(CH_3)_2$ group leads to vanishing contributions to the energies of the ground and Franck-Condon excited state.

The above results are consistent with the experimental data of Groenen and Koelman [19] who also investigated the electro-optical absorption of Michler's ketone. The evaluation of their data has been based on moments analysis assuming C_2 symmetry of the molecule and therefore prohibits the estimation of the angle between μ_{gG} and μ_{aG}. A comparison of the evaluation based on moments analysis [20] and the evaluation based on (6), using estimated values of t_G^* and u_G^* obtained from the measured spectra, has shown that generally the latter method does not only give more detailed information, but also leads to data with better statistical significance [21].

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