k_d and $k_d/k_{dis} = 10^2\ M^{-1}$, the latter relation being roughly estimated from the phosphorescence spectral data. Obviously, the experimental results agree, at least qualitatively, with the curve 2 rather than with the curve 1. It is thus concluded that the self-quenching pathway, namely, the quenching by the ground state of the solute molecule is likely to participate in the deactivation of the triplet state.

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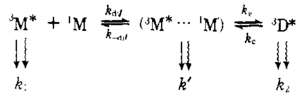

where k_{-dif} denotes the diffusion-controlled rate constant for dissociation of the encounter complex, ($^3M^* \cdots {}^1M$). Under the conditions of $k_{-dif} \gg k_e$, k', the rate constants in (6) are expressed as $k_1' = \gamma k'$, $k_d = \gamma k_e$, and $k_{dis} = k_c$, with $\gamma = k_{dif}/k_{-dif}$.

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The Optical Activity of Low-Symmetry Ketones in Absorption and Emission

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Abstract: The optical activity in the n → π^* transition of a series of ketones is studied in absorption and emission. For a number of ketones the comparison of the experimental CD and CPL spectra reveals marked differences: both the magnitude of the integrated optical activity and the band shape may be utterly different in absorption and emission. In this paper a relation is laid between these phenomena. The often large discrepancy between the value of the rotational strength in absorption and fluorescence (for some compounds up to sign) points to a large distortion of the $^1n\pi^*$ state of ketones with respect to their ground state. On the other hand it is shown from general principles that a negative value of the ratio R^{abs}/R^{em} requires a change of sign in either the CD or the CPL curve, i.e., can cause a bisignate Cotton effect. To get a better insight in the observed phenomena, a model is constructed to predict the qualitative band forms of the CD and CPL. Based on the large shift in equilibrium geometry between ground and excited state, the model makes use of an expansion of the electronic rotational strength about those points of normal coordinate space where the Franck-Condon overlap for a particular vibronic transition is peaked. When a linear relationship between the rotational strength and one normal coordinate is assumed, the observed band shapes of CD and CPL of the ketones studied can be successfully explained. In addition to a better understanding of the origins of bisignate Cotton effects, this study leads to the conclusion that the optical activity in the n → π^* transition of ketones still can be understood with the relatively simple theory of Moffitt and Moscowitz, provided proper allowance is made for a legitimate role of the excited state.

The optical activity of an electronic transition is governed by its rotational strength,[2] which in turn is defined by the scalar product of the quantum mechanical electric and magnetic dipole transition moments. The molecular wave functions, incorporated in the integrands of the spectral transition moments, depend heavily on the nuclear coordinates and thus a connection between optical activity and molecular geometry is laid—at least in principle, for the actual road leading from experimental circular dichroism (CD) to molecular architecture is sometimes long and slippery owing to the well-known difficulties encountered in finding satisfactory wave functions. It is not surprising therefore that chemists have tried to find other, easier routes and often with considerable success. We refer here to the many well-known sector rules which correlate in an empirical way the contributions to the optical activity of the separate atoms and their relative positions in a molecule. One of the most famous sector rules is the octant rule for chiral ketones,[3] which has proven to be extremely useful, e.g., in the field of conformational analysis.[4] Notwithstanding the generally greater accuracy and applicability of diffraction methods and NMR techniques in the elucidation of molecular structures, it is in particular these sector rules which permit one to consider the study of optical activity as an indispensable tool in structural chemistry, this being more so since it recently turned out to be possible to measure the optical activity of excited species[5] (circular polarization of luminescence, CPL). While circular dichroism provides information on the chirality of the molecule in its ground state, the CPL incorporates the essential features of the structure in the excited state. This information, emitted by the fluorescent or phosphorescent molecule by means of unequal amounts of right and left circularly polarized radiation, in general cannot be detected that easily by other techniques. The potential value of the CPL technique can perhaps be appreciated even more when realizing that a confrontation of CD and CPL provides the *change* of the rotatory strength brought about by the *change* in conformation upon excitation. In a way this is the leading thought in our discussions later on.

As will be shown below, the electronic rotational strength, obtainable from the experimental CD by integrating over all its vibrational fine structure, is a quantity which pertains to the equilibrium geometry of the molecule in its vibronic ground state. When this ground state is not chiral, a zero electronic rotational strength should be observed. Perhaps this situation is approached in the case of (1R)-[2-^{18}O]-α-fenchocampheronequinone[6] whose optical activity is due to the incorporation of one ^{18}O atom in the cis α-diketone moiety. The fact that the integrated CD in the visible absorption band approaches zero is in accordance with the expectation that the structures of molecules with ^{18}O resp. ^{16}O in them, will not be very different.[7] However, while the integrated ellipticity is very small, the ellipticity itself is not, reaching appreciable positive and negative values at various wavelengths. Apparently in this compound the molecular vibrations monopolize the generation of optical activity. But also in other cases, e.g., in ketones of the types studied in this paper, vibrations do try to appropriate appreciable parts of the ellipticity, and it is of interest to see how successful they are. The study of the vibronic optical activity of ketones is of particular importance in connection to the controversy which arose when Weigang[8] suggested—contrary to the implications of the theory of Moffitt and Moscowitz[9]—that the integrated CD of ketones might contain a large contribution entirely due to vibrations, i.e., deviations from equilibrium geometry. Weigang put forward his theory to explain the occurrence of CD curves, which cross zero within an absorption band (to describe such curves, Klyne and Kirk[10] coined the term "bisignate"). According to Weigang, the short wavelength lobe of a bisignate CD curve is of purely vibrational origin while the long wavelength branch contains the optical activity due to static molecular structure.

We have measured the optical activity of a number of ketones, not only in absorption but also in the fluorescence. The new information that is acquired from the emission experiments shall give us the opportunity to verify a qualitative theory which we put forward to account for the occurrence or absence of bisignate Cotton effects in absorption and emission, and which shows that bisignate Cotton effects can be perfectly well explained with the theory of Moffitt and Moscowitz.

The organization of this paper is as follows. After having discussed the relationship between experimental and theoretical quantities (part 1) we report and discuss in part 2 the CD and CPL spectra of a number of saturated ketones. In part 3 we present a theory on the mechanism by which the optical activity in an absorption band is generated as a function of excitation energy; this will enable us to explain qualitatively the shapes of the observed CD and CPL spectra and to learn more about the origin of bisignate Cotton effects.

1. Relationship between Experimental and Theoretical Quantities

If ϵ_L (ϵ_R) is the molecular decadic extinction coefficient measured with left (right) circularly polarized light the familiar relations[11] (eq 1 and 2) connect the dipole strength D and rotational strength R of a given absorption band with its absorbance and circular dichroism:

$$D = 92.0 \times 10^{-40} \int_{\text{band}} \frac{\epsilon_L + \epsilon_R}{2} \frac{d\nu}{\nu} = 92.0 \times 10^{-40} \int_{\text{band}} \frac{\epsilon}{\nu} d\nu \qquad (1)$$

$$R = 23.0 \times 10^{-40} \int_{\text{band}} (\epsilon_L - \epsilon_R) \frac{d\nu}{\nu} = 23.0 \times 10^{-40} \int_{\text{band}} \frac{\Delta\epsilon}{\nu} d\nu \qquad (2)$$

(D and R are expressed in cgs units). From experiment a dissymmetry factor can be defined as

$$g(\nu) = \frac{\Delta\epsilon(\nu)}{\epsilon(\nu)} \qquad (3)$$

The dissymmetry factor for the entire band is given by

$$g = \frac{4R}{D} = \frac{\int_{\text{band}} \frac{\Delta\epsilon}{\nu} d\nu}{\int_{\text{band}} \frac{\epsilon}{\nu} d\nu} \qquad (4)$$

and it follows that if absorption and CD have similar band shapes, the two g factors are identical.

The measurement of the circular polarization of the luminescence in many respects is the emission analogue of a circular dichroism experiment. When a sufficiently high concentration of molecules in their fluorescent state can be created, e.g., by irradiation with unpolarized light, the amount of photons of the two circular polarization states in the spontaneous emission will be different, provided the fluorescent species are chiral. So one defines[5]

$$\Delta I(\nu) = I_L(\nu) - I_R(\nu) \qquad (5)$$

where $I_L(I_R)$ is the intensity of the part of the emission which is left (right) circularly polarized (in relative quanta per unit of frequency interval). The mean intensity of the fluorescence is given by

$$I(\nu) = \frac{I_L(\nu) + I_R(\nu)}{2} \qquad (6)$$

while the dissymmetry factor takes the form

$$g_{\text{lum}}(\nu) = \frac{\Delta I(\nu)}{I(\nu)} \qquad (7)$$

For a given electronic transition the relations between the experimental and theoretical quantities are[5]

$$R^{\text{em}} = c \int_{\text{band}} \frac{\Delta I}{\nu^3} d\nu \qquad (8)$$

$$D^{\text{em}} = c \int_{\text{band}} \frac{I}{\nu^3} d\nu \qquad (9)$$

where c is a constant. Unlike in absorption the values of D and R in emission usually are not obtained separately since in the fluorescence experiment only the relative intensity distribution $I(\nu)$ is measured and thus the value of c in eq 8 and 9 is not known. However, since the g value for the luminescence band is available, knowledge of the value of D^{em}—obtainable, e.g., from a determination of the radiative lifetime of the upper state—leads to R^{em}.

$$g_{\text{lum}} = \frac{\int_{\text{band}} \frac{\Delta I}{\nu^3} d\nu}{\int_{\text{band}} \frac{I}{\nu^3} d\nu} = \frac{4R^{\text{em}}}{D^{\text{em}}} \qquad (10)$$

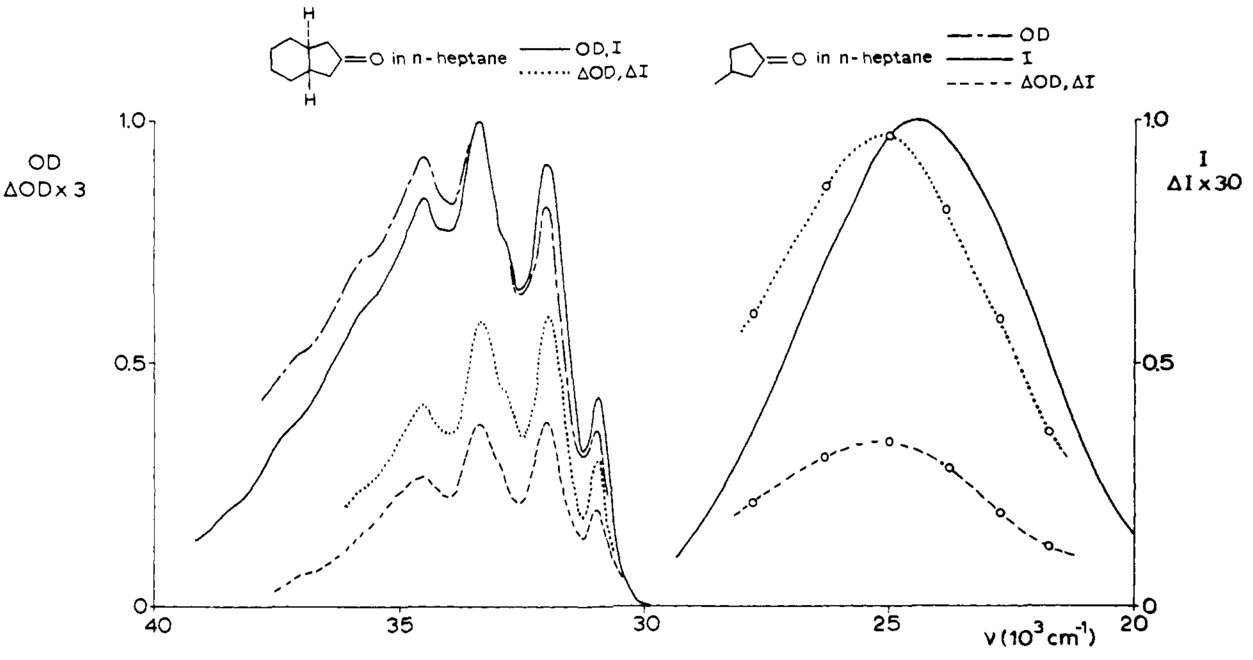


Figure 1. β-Hydrindanone and 3-methylcyclopentanone: left, unpolarized absorption (OD) and circular dichroism (ΔOD); right, unpolarized fluorescence (I) and CPL (ΔI). The fluorescence curves for both compounds coincide. Note that the scale factors for ΔOD and ΔI are different.

Experimental Section

The CD spectra were taken with a Jouan Dichrographe and the absorption spectra with a Cary 15 spectrophotometer. The measurement of the ΔI and I curves proceeded as follows.[12] The excitation beam is obtained from a 900-W xenon arc and a Bausch and Lomb "high intensity" monochromator. Before passing through the emission monochromator (Bausch and Lomb "high intensity") the circular polarization of the fluorescence ΔI is modulated at a frequency of 50 kHz by an acoustooptic modulator (Morvue) followed by a linear polarizer (Polacoat). The CPL is detected as ac photocurrent, the total luminescence I as dc photocurrent. Depending on the intensity of the emission available, our spectrometer detects $\Delta I/I$ values of 10^{-3} to 10^{-4}.

For all compounds the absorbance OD, the differential absorbance ΔOD, the fluorescence I, and the circular polarization of the fluorescence ΔI were measured using the same sample solution. In the figures the maxima of the curves for OD and I are always put equal to 1. When during the measurement the composition of the solution changed—e.g., because of photoracemization or other photoreactions—the experiment was (more quickly) repeated with a fresh solution. In all compounds examined, the fluorescence proved to be a broad, structureless band, the CPL of which was determined using a 15-nm spectral band width. All measurements were performed at room temperature. Epiandrosterone was obtained commercially (Fluka), the other ketones were put at our disposal by Dr. W. C. M. C. Kokke, formerly at this department.

2. Discussion of the CPL Spectra

(a) ***trans*-β-Hydrindanone.** The CPL spectrum of *trans*-β-hydrindanone, a ketone with C_2 symmetry (cf. Figure 1), is in essential agreement with that reported by Emeis.[11] In comparing CPL and CD one observes a drastic lowering of the dissymmetry factor in the fluorescence band relative to that in the absorption band. As shown by Emeis, this points to an excited state in which the nuclear configuration around the carbon atom of the carbonyl group is pyramidal: in the $^1n\pi^*$ state the C-O bond is no longer directed along the $-z$ axis but, while still being in the yz plane, intersects at an angle ϕ or $-\phi$ with it (see for the molecular reference frame Figure 2).

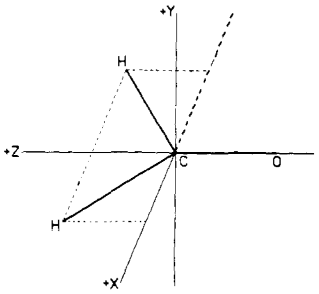


Figure 2. Reference frame for formaldehyde (and ketones).

Whereas in the ground state conformation the electric dipole transition moment is directed along the z axis, in the two pyramidal configurations (that are identical) the transition is allowed in the x direction too. Hence the dipole strength is larger in emission than in absorption. However, since it is unlikely that the value of the z component of the electric dipole transition moment changes much upon excitation, and as calculations show that the z component of the magnetic dipole transition moment in emission has about the same magnitude as in absorption, the rotational strengths in absorption and fluorescence are probably not very different (the x-polarized intensity in emission does not carry rotational strength because μ_x is zero). Hence Emeis could conclude that the lowering of the dissymmetry factor upon excitation is primarily due to an increase of the dipole strength.

(b) **Low-Symmetry Ketones.** With regard to shape and magnitude, the CD spectrum of 3-methylcyclopentanone (Figure 1) strongly resembles that of hydrindanone. This is not surprising as calculations[11b,13] indicate that the circular dichroism of cyclopentanone derivatives is caused more by the chirality of the cyclopentanone ring itself than by the chiral disposition of its substituents. Therefore, the fact that 3-methylcyclopentanone does not possess a C_2 axis does not exclude a close analogy with hydrindanone,[14] and perhaps the same argument holds—albeit to a lesser extent—for 2,2,3-trimethylcyclopentanone (Figure 3a).

This should imply that with these compounds the lowering of the anisotropy factor which is observed in CPL should be ascribed more to an increase of the dipole strength in emission as compared to absorption, than to a change of the rotational strength. However, from our experimental data on other compounds it emerges that, in general, matters are more complex. In the case of camphor (Figure 3b) the CPL appears to change sign within the emission band. This phenomenon reminded us of analogous situations in absorption where sometimes the CD in the n → π^* band changes sign and prompted us to measure the CPL spectra of isofenchone and camphenilone. In methanol as well as in *n*-heptane camphenilone exhibits a bisignate CD curve, while in emission the Cotton effect has one sign (Figure 3e). Also isofenchone (Figure 3f) shows in absorption a bisignate Cotton effect which, incidentally, is very sensitive towards solvent. In emission there is also a bisignate Cotton effect if the solvent is *n*-heptane, but not when it is methanol. Other ketones in the bicycloheptanone series, 5-ketoborneol (Figure 3c), 5-ketobornyl acetate (Figure 3g), and 6-ketobornyl acetate (Figure 3d), behave normally in the sense that no bisignate Cotton effects are observed and that CD and CPL have the same sign, but the optical activity of α-fenchocampherone changes sign again at the extreme low energy side of the emission band (Figure 3h). That the occurrence of bisignate Cotton effects is not restricted to compounds in the norcamphor series is shown by the spectra of epiandrosterone (Figure 3i).

In summary, if one compares the optical activities in emission and absorption the most striking feature which emerges is that the absolute value of the dissymmetry factor in emission is smaller (often much smaller) than in absorption, the ratio g_{lum}/g being far from constant in the series of compounds investigated. Furthermore it appears that a bisignate Cotton effect in absorption may or may not be accompanied by a bisignate one in emission, and the same holds for a normal CD curve. With all the differences which exist between the CD and CPL spectra of the examined ketones, in one respect they all agree: in no case are the sign of the CD at higher wavelengths and the sign of the CPL at shorter wavelengths (i.e., near the (o,o) band of the electronic transition) different. In part 3 we shall examine these various observations more closely. It then will appear that the bisignate Cotton effects in absorption and emission take a key position in the explanation of the observed phenomena.

3. Band Shapes of CD and CPL

(a) General. In the Born–Oppenheimer approximation, the rotational strength of a transition from the vibronic ground state Oo to a vibrational level $\bar{n}$ of the excited electronic state N is given by[4]

$$R_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{n}}} = Im(\mathrm{Oo}|\mathbf{r}|\mathrm{N}\bar{\mathrm{n}})\cdot(\mathrm{N}\bar{\mathrm{n}}|\boldsymbol{\mu}|\mathrm{Oo}) \qquad (11)$$

while the expression for the dipole strength reads

$$D_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{n}}} = |(\mathrm{Oo}|\mathbf{r}|\mathrm{N}\bar{\mathrm{n}})|^2 \qquad (12)$$

In these formulas Kk stands for a product function $\Psi_{\mathrm{K}}(r,Q)\chi_{\mathrm{k}}{}^{\mathrm{K}}(Q)$ of an electronic wave function Ψ_{K}, depending parametrically on the nuclear coordinates Q, and a vibrational wave function $\chi_{\mathrm{k}}{}^{\mathrm{K}}$, which depends only on the normal coordinates in the electronic state K.

Throughout this paper we shall use capital letters to denote electronic wave functions and small ones to denote vibrational functions. Vibrational wave functions which are associated with the excited electronic state will be indicated with a bar. As we intend to deal with nondegenerate states only, all wave functions will be taken real.

Performing in eq 11 and 12 the integration over electronic coordinates one has

$$R_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{n}}} = Im(\mathrm{o}|\mathbf{r}_{\mathrm{ON}}(Q_1,Q_2,\ldots\ldots,Q_{3M-6})|\bar{\mathrm{n}}) \cdot(\bar{\mathrm{n}}|\boldsymbol{\mu}_{\mathrm{NO}}(Q_1,Q_2,\ldots\ldots,Q_{3M-6})|\mathrm{o}) \qquad (11\mathrm{a})$$

and

$$D_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{n}}} = |(\mathrm{o}|\mathbf{r}_{\mathrm{ON}}(Q_1,Q_2,\ldots\ldots,Q_{3M-6})|\bar{\mathrm{n}})|^2 \qquad (12\mathrm{a})$$

where the electronic matrix elements $\mathbf{r}_{\mathrm{ON}}$ and $\boldsymbol{\mu}_{\mathrm{NO}}$ are functions in the $(3M - 6)$ dimensional space of nuclear coordinates (M is the number of nuclei in the molecule).

Analogously, if in emission the initial state is denoted by N$\bar{\mathrm{o}}$ and the final one by On, it is convenient to define[16] the rotational strength in this transition as

$$R_{\mathrm{N}\bar{\mathrm{o}}\rightarrow\mathrm{On}} = Im(\mathrm{On}|\mathbf{r}|\mathrm{N}\bar{\mathrm{o}})(\mathrm{N}\bar{\mathrm{o}}|\boldsymbol{\mu}|\mathrm{On}) = Im(\mathrm{n}|\mathbf{r}_{\mathrm{ON}}(Q_1,Q_2,\ldots\ldots,Q_{3M-6})|\bar{\mathrm{o}}) \cdot(\bar{\mathrm{o}}|\boldsymbol{\mu}_{\mathrm{NO}}(Q_1,Q_2,\ldots\ldots,Q_{3M-6})|\mathrm{n}) \qquad (13)$$

whereas we have for its dipole strength

$$D_{\mathrm{N}\bar{\mathrm{o}}\rightarrow\mathrm{On}} = |(\bar{\mathrm{o}}|\mathbf{r}_{\mathrm{NO}}(Q_1,Q_2,\ldots\ldots,Q_{3M-6})|\mathrm{n})|^2 \qquad (14)$$

From the above equations, which hold quite generally, one can draw some important conclusions.

Firstly, from a comparison of eq 11a and 13 it follows that the rotatory strength of the (o,o) transition in absorption is identical to that in the (o,o) emission band, and a similar conclusion is reached for the dipole strengths of both transitions.

$$R_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{o}}} = R_{\mathrm{N}\bar{\mathrm{o}}\rightarrow\mathrm{Oo}} \qquad (15)$$

$$D_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{o}}} = D_{\mathrm{N}\bar{\mathrm{o}}\rightarrow\mathrm{Oo}} \qquad (16)$$

These relations, which are rather trivial for a molecule in the gas phase, do not necessarily hold if in between the processes of absorption and emission the nature of the species changes—e.g., because of a different solvation in the excited state. In that case the initial and final states of the absorbing species are no longer identical with the final and initial states of the fluorescent species, and relations 15 and 16 may break down. Later on in this section we shall briefly refer to this point.

Secondly, application of the quantum mechanical sum rule to eq 11a, 12a, 13, and 14 yields the expressions for the total rotational and dipole strengths in absorption and emission.

$$R^{\mathrm{abs}} = \sum_{\bar{\mathrm{n}}} R_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{n}}} = Im(\mathrm{o}|\mathbf{r}_{\mathrm{ON}}(Q_1,\ldots)\cdot\boldsymbol{\mu}_{\mathrm{NO}}(Q_1,\ldots)|\mathrm{o}) = (\mathrm{o}|R_{\mathrm{ON}}(Q_1,\ldots)|\mathrm{o}) \qquad (17)$$

$$D^{\mathrm{abs}} = \sum_{\bar{\mathrm{n}}} D_{\mathrm{Oo}\rightarrow\mathrm{N}\bar{\mathrm{n}}} = (\mathrm{o}|D_{\mathrm{ON}}(Q_1,\ldots)|\mathrm{o}) \qquad (18)$$

$$R^{\mathrm{em}} = \sum_{\mathrm{n}} R_{\mathrm{N}\bar{\mathrm{o}}\rightarrow\mathrm{On}} = (\bar{\mathrm{o}}|R_{\mathrm{NO}}(Q_1,\ldots)|\bar{\mathrm{o}}) \qquad (19)$$

$$D^{\mathrm{em}} = \sum_{\mathrm{n}} D_{\mathrm{N}\bar{\mathrm{o}}\rightarrow\mathrm{On}} = (\bar{\mathrm{o}}|D_{\mathrm{NO}}(Q_1,\ldots)|\bar{\mathrm{o}}) \qquad (20)$$

The variables Q_r in the electronic matrix elements $\mathbf{r}_{\mathrm{ON}}(\ldots\ldots Q_r\ldots\ldots)$ and $\mu_{\mathrm{NO}}(\ldots\ldots Q_r\ldots\ldots)$ refer to the nuclear normal coordinates in the ground state in eq 17 and 18, and to the normal coordinates of the excited state in eq 19 and 20. The vibrational wave functions of the ground state, o and n, are taken to be products of one-dimensional vibrational wave functions in the variables $Q_r - Q_r{}^\circ$, where $Q_r{}^\circ$ is the expectation value of Q_r in the vibronic ground state Oo. That is

$$\mathrm{o} = \mathrm{o}_1(Q_1 - Q_1{}^\circ)\mathrm{o}_2(Q_2 - Q_2{}^\circ)\ldots\ldots\mathrm{o}_r(Q_r - Q_r{}^\circ) \qquad (21)$$

and the form of n is similar, but with one or more elementary vibrations excited. Likewise the vibrational wave functions of the excited state consist of a product of $3M - 6$ one-dimensional vibrations in the normal coordinates of the

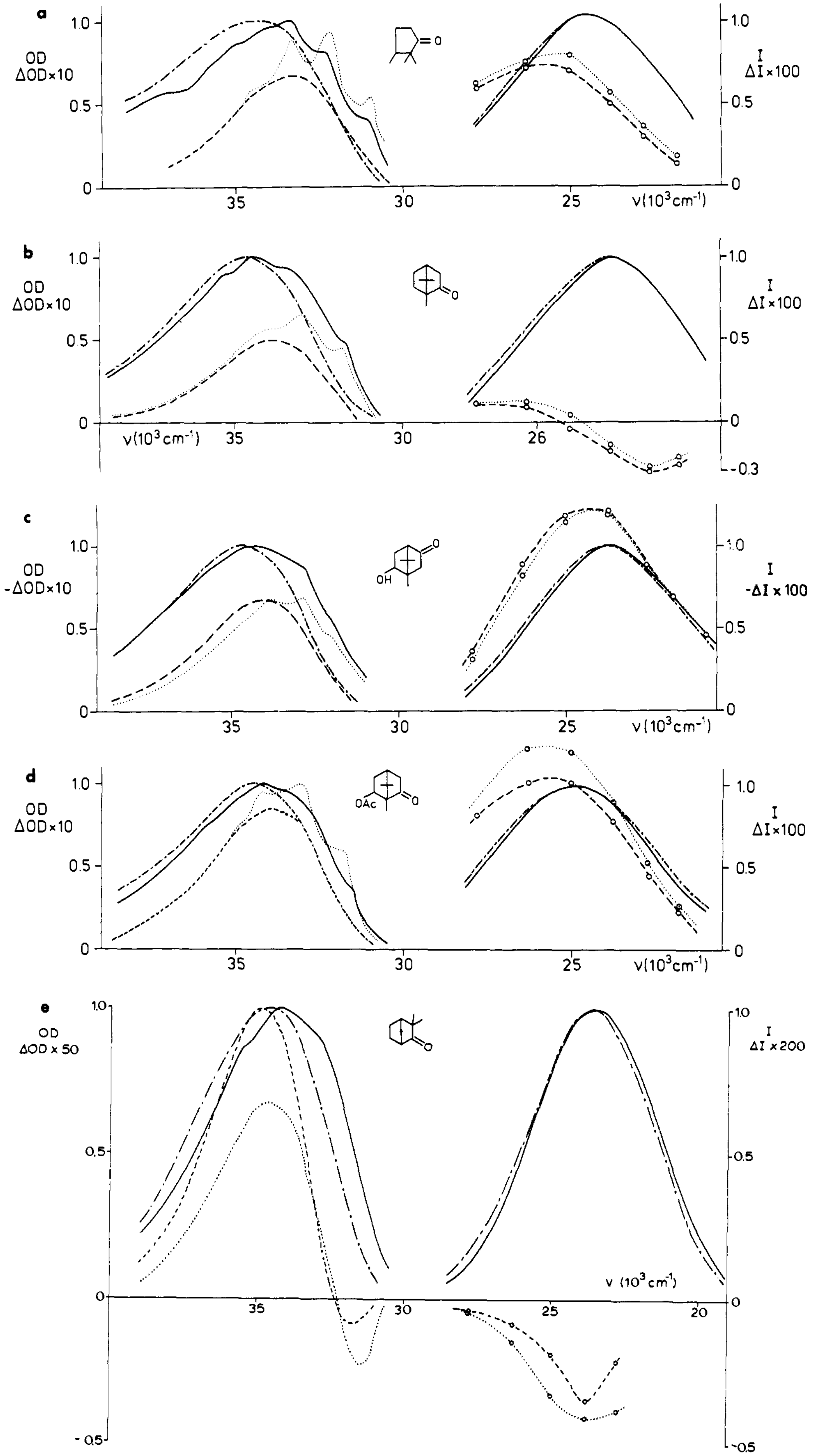
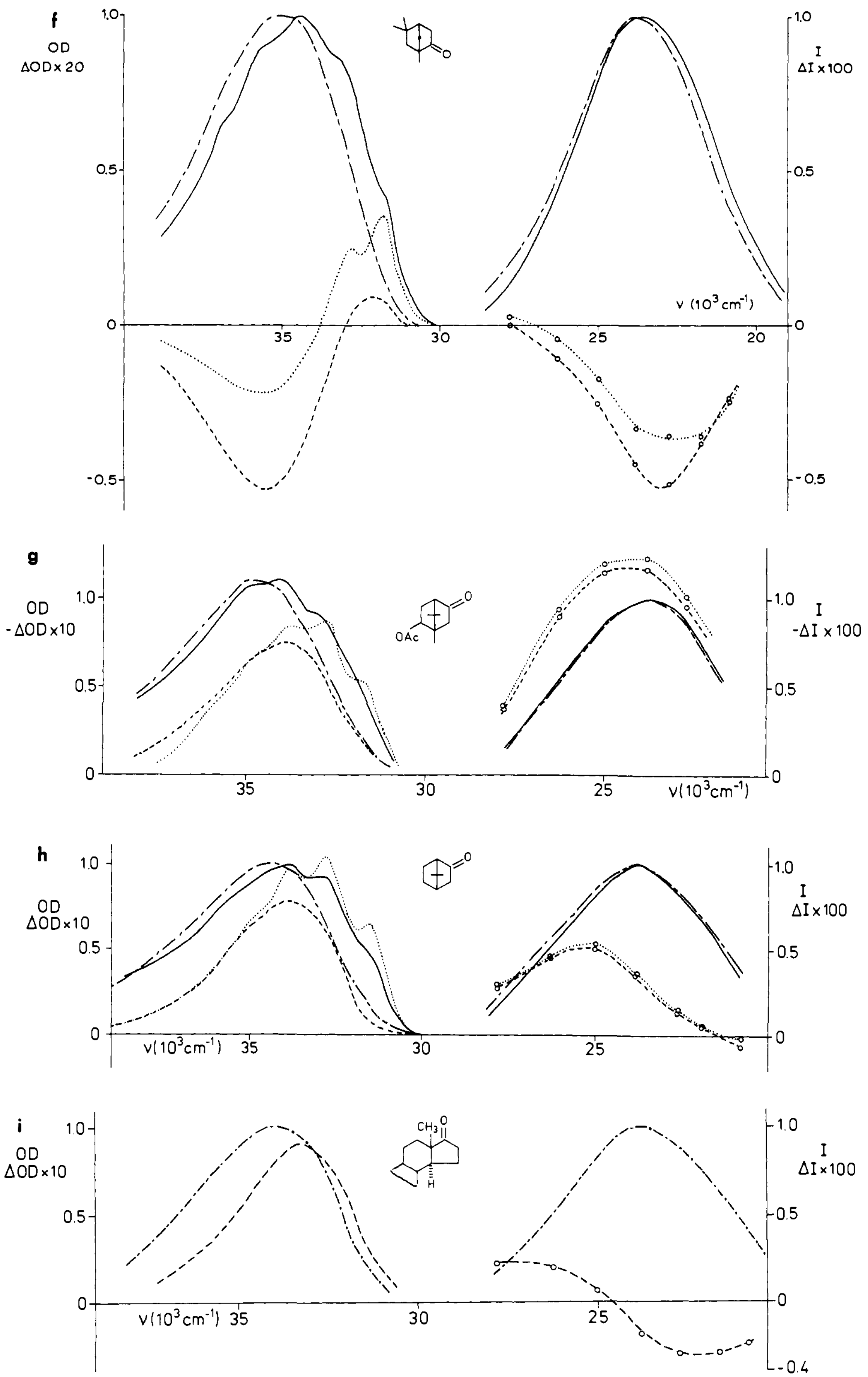


Figure 3. Spectra of 2,2,3-trimethylcyclopentanone (a), camphor (b), 5-ketoborneol (c), 6-ketobornyl acetate (d), camphenilone (e), isofenchone



(f), 5-ketobornyl acetate (g), α-fenchocampherone (h), and epiandrosterone (i): (—) unpolarized absorption (OD) and fluorescence (*I*) in *n*-heptane, (···) CD (ΔOD) and CPL (Δ*I*) in *n*-heptane, (- -) OD and *I* in methanol, (- - -) ΔOD and ΔI in methanol.

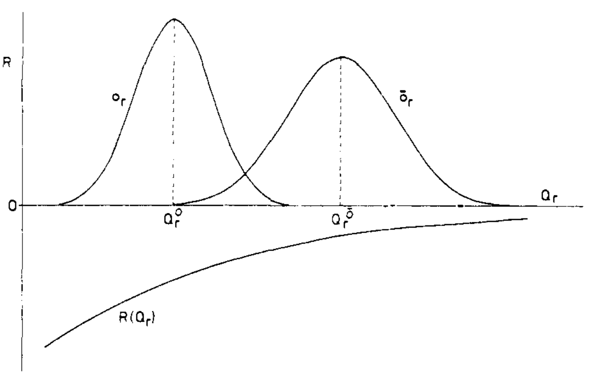


Figure 4. One-dimensional zero-point-vibrational wave functions in ground and excited state. Variation of electronic rotational strength with Q_r.

upper state. When neglecting mode mixing, the normal coordinates of ground and excited state are equal whence we have

$$\bar{o} = \bar{o}_1(Q_1 - \bar{Q}_1{}^\circ)\bar{o}_2(Q_2 - \bar{Q}_2{}^\circ)\ldots\ldots\bar{o}_r(Q_r - \bar{Q}_r{}^\circ) \tag{22}$$

and an analogous expression for $\bar{n}$. The bars in $\bar{o}_r$ and $\bar{Q}_r{}^\circ$ indicate that both shape and center of the vibrational wave functions in the upper state differ from those in the ground state. It will appear later that the large value of $Q_r{}^\circ - \bar{Q}_r{}^\circ$ in ketones gives us a clue to a better understanding of their optical activity. To illustrate this, we assume for a moment that R_{ON} depends on one Q_r. The total rotational strength in absorption is given by

$$R^{\mathrm{abs}} = (o|R(Q)|o) = (o_1|o_1)(o_2|o_2)\ldots(o_r|R(Q_r)|o_r)\ldots = (o_r|R(Q_r)|o_r) \tag{23}$$

meaning that $R(Q_r)$ has to be averaged with the distribution function $o_r{}^2$. Similarly R^{em} is found from the rotational strength function by weighting it with $\bar{o}_r{}^2$. In the situation, represented by Figure 4, both rotational strengths are therefore negative, the absolute value of R^{abs} being larger than that of R^{em}. It also follows that, in general, R^{abs} will be equal to R^{em} only if the vibrational functions o and $\bar{o}$ are identical, or if R does not depend on Q_r.

Before further elaborating on eq 15-20 we first discuss the consequences of a confrontation of these basic equations with experiment. We recall that the quantum mechanical quantities R^{abs} and D^{abs} are accessible from experiment through the relations (1) and (2), but that from an actual CPL measurement only the value of $4R^{\mathrm{em}}/D^{\mathrm{em}}$ is found, not those of R^{em} and D^{em} separately (cf. eq 8-10). This means, that in order to be able to compare the magnitudes of R^{abs} and R^{em}, we first have to know D^{em}. However, in those cases where g and g_{lum} are opposite in sign, we immediately can conclude—without knowing the exact value of D^{em}—that the rotational strengths in absorption and fluorescence are quite different. This situation actually occurs for camphor (Figure 3b), camphenilone (Figure 3e), and epiandrosterone (Figure 3i).

As regards the experimental values of the rotational strengths in the (o,o) bands of absorption and fluorescence the following may be remarked. Although in chiral ketones the (o,o) transition is never symmetry forbidden, its intensity is still weak because of a small Franck-Condon factor. Besides, were it not for this reason, the (o,o) band would not be easily observable as such because of the lack of fine structure in the spectra. However, with the assumption that on the one hand the sign of the CD at the extreme long wavelength side of the absorption band agrees with that in the (o,o) transition and on the other hand the sign of ΔI near the intersection region of the fluorescence and absorption curves corresponds with that in the (o,o) emission band, the signs of the rotational strengths of the (o,o) bands in absorption and emission are available. From the experimental spectra it then follows that indeed the signs of the optical activities of the (o,o) transitions in fluorescence and absorption are identical, one possible exception being constituted by isofenchone in methanol solution (Figure 3f), where the CPL value at short wavelengths is zero. However, in view of the extremely large solvent dependence of the total rotational strength of this compound (compare the CD curves in *n*-heptane and methanol), we here probably encounter a case in which the role of the solvent molecules in the generation of optical activity cannot be neglected.

Having found no indication (except for isofenchone) that the solvent enters the rotational strength in a decisive way, we can now consider in more detail the rotational strength of the individual vibronic transitions. Before doing so we notice that a negative ratio $R^{\mathrm{abs}}/R^{\mathrm{em}}$ has a very interesting implication. In connection with the fact that the rotational strength in the (o,o) transition in absorption and emission must have equal sign, a negative ratio $R^{\mathrm{abs}}/R^{\mathrm{em}}$ requires a change of sign to occur in the CD or in the CPL spectrum. At this stage, however, we neither know where in the frequency scale the change of sign takes place nor do we know whether there is only one such change. To answer these questions we shall design in the next section a formalism to describe the rotational strengths in vibronic transitions, which will allow us to draw in part 3c more pertinent conclusions about the band shapes of CD and CPL. In these discussions we shall lean heavily on the fact that the equilibrium geometry of ketones in ground and $^1n\pi^*$ states is quite different (which may be concluded from the large discrepancies between the observed values of R^{abs} and R^{em}).

(b) The Rotational Strength in Vibronic Transitions. We assume that the quantities $\mathbf{r}_{\mathrm{ON}}(Q)$ and $\mu_{\mathrm{NO}}(Q)$ vary at most linearly with the Q_r. This implies that we may cut off their expansions around some fixed point $\tilde{Q} = (\tilde{Q}_1, \tilde{Q}_2, \ldots\ldots, \tilde{Q}_{3M-6})$ after the second term.

$$(o|\mathbf{r}_{\mathrm{ON}}(Q)|\bar{n}) = (o|\mathbf{r}_{\mathrm{ON}}(\tilde{Q})|\bar{n}) + (o|\sum_r (Q_r - \tilde{Q}_r)\mathbf{r}_{\mathrm{ON}}{}^{(1)r}|\bar{n}) \tag{24}$$

$$(\bar{n}|\mu_{\mathrm{NO}}(Q)|o) = (\bar{n}|\mu_{\mathrm{NO}}(\tilde{Q})|o) + (\bar{n}|\sum_r (Q_r - \tilde{Q}_r)\mu_{\mathrm{NO}}{}^{(1)r}|o) \tag{25}$$

where

$$\mathbf{r}_{\mathrm{ON}}{}^{(1)r} = \left.\frac{\partial \mathbf{r}_{\mathrm{ON}}(Q)}{\partial Q_r}\right|_{Q=\tilde{Q}} \tag{26}$$

and

$$\mu_{\mathrm{NO}}{}^{(1)r} = \left.\frac{\partial \mu_{\mathrm{NO}}(Q)}{\partial Q_r}\right|_{Q=\tilde{Q}} \tag{27}$$

Usually[9,8] $\tilde{Q}$ is taken equal to Q°, the equilibrium geometry in the vibronic ground state. In view, however, of the large differences in equilibrium geometry in the ground and $^1n\pi^*$ states of ketones, the following alternative may be fruitful. Consider an integral such as $(o|\mathbf{r}_{\mathrm{ON}}(Q)|\bar{n})$. The integrand of this matrix element, consisting of a product of the function $\mathbf{r}_{\mathrm{ON}}(Q)$ and the vibrational transition density $o(Q)\bar{n}(Q)$, can have appreciable values only at those points Q where the product $o\bar{n}$ is different from zero. This immediately suggests an expansion of $\mathbf{r}_{\mathrm{ON}}(Q)$ at a point in Q space where $o\bar{n}$ is peaked. Therefore we shall take $\tilde{Q}$ equal to $Q^{o\bar{n}}$, where $Q^{o\bar{n}}$ is obtained by weighting the nuclear position vector with the distribution function $o\bar{n}$,

$$Q_r^{o\bar{n}} = \frac{(o|Q_r|\bar{n})}{(o|\bar{n})} \tag{28}$$

where $r = 1, 2, \ldots, 3M - 6$. Note that different n give rise to different values of $Q^{o\bar{n}}$.[17] With eq 28 the expansions of eq 24 and 25 transform to

$$(o|\mathbf{r}_{ON}(Q)|\bar{n}) = \mathbf{r}_{ON}(Q^{o\bar{n}})(o|\bar{n}) \tag{29}$$

$$(\bar{n}|\mu_{NO}(Q)|o) = \mu_{NO}(Q^{o\bar{n}})(\bar{n}|o) \tag{30}$$

whereas the expression for the rotational strength in the transition Oo → N$\bar{n}$ takes the form

$$R_{Oo\rightarrow N\bar{n}} = Im\,\mathbf{r}_{ON}(Q^{o\bar{n}})\mu_{NO}(Q^{o\bar{n}})(o|\bar{n})(\bar{n}|o) = R_{ON}(Q^{o\bar{n}})(o|\bar{n})^2 \tag{31}$$

From eq 31 we see that the vibronic rotatory strength is equal to the electronic rotational strength evaluated at the point $Q^{o\bar{n}}$, times a Franck-Condon factor.

Before using eq 31 to study the band shapes of CD and CPL, we emphasize that the expansion leading to eq 29-31 is not always warranted. It is obvious that its utility depends heavily on the shape of the vibrational overlap density $o\bar{n}$. If $o\bar{n}$ is a capricious function consisting of many large peaks at various positions on the Q scale, the value of an integrand such as $o(Q)\mathbf{r}_{ON}(Q)\bar{n}(Q)$ is not predominantly determined by its value in a restricted region around one point Q. In this case—which would arise if o and $\bar{n}$ were centered around the same point Q—there is no advantage in expanding the matrix element $(o|\mathbf{r}_{ON}(Q)|\bar{n})$ around $Q^{o\bar{n}}$. With ketones, however, there is a large separation between the centers of o and $\bar{n}$, and one may expect that to a good approximation $o\bar{n}$ has one dominating peak in Q space.

There is still another argument which underlines the relevance of eq 31 in the interpretation of the experimental spectra of ketones: when upon excitation the molecule is distorted in the direction Q_r, one will observe in the spectrum particularly progressions in those vibrations that are based on the normal coordinate Q_r.

(c) Band Shapes of CD and CPL. We assume that the electronic rotational strength in eq 31 depends on one normal coordinate Q_r and moreover that the experimental CD and CPL spectra arise predominantly from progressions in normal modes corresponding to this Q_r. Then a transparent connection may be laid between R as a function of Q and the experimental CD and CPL as a function of frequency. This is illustrated in Figure 5. The rotational strength in the (o,o) transition is $R(Q^{o\bar{o}})(o|\bar{o})^2$. In vibrational transitions o → $\bar{n}$ one proceeds towards the left on the Q scale as $\bar{n}$ increases and to higher frequencies in the CD spectrum. In emission one deals with transitions $\bar{o}$ → n. The higher the n, the lower the frequency and the larger the value of $Q^{\bar{o}n}$. Since in the construction of Figure 5 the necessary Franck-Condon factors are guessed and the relation of Q and ν is not necessarily linear, the figure expresses a merely qualitative relationship between $R(Q)$ and the magnitude of the CD and CPL as a function of frequency.

We are now ready for a comparison of experimental data and theory. As mentioned, the determination of the absolute magnitude of R^{em} is hampered by not knowing the value of D^{em}. From the ratio g/g_{lum} which is obtainable from the observed spectra, however, we can deduce the value of R^{abs}/R^{em} when we assume that $D^{em} = cD^{abs}$, where c is a constant for all ketones. The latter approximation probably is not that unrealistic; the highly localized nature of the n → π* transition causes transition energies, bandwidths, and extinction coefficients for aliphatic ketones to be very similar and it is conceivable that a similar argument holds for the reverse transition as well. Since it can be argued that for hydrindanone $R^{abs} \approx R^{em}$ (cf. part 2a), implying that here $D^{em} \approx 5D^{abs}$, we tentatively take $c = 5$ for all ketones. Then the compounds we have measured, when classified according to their R^{abs}/R^{em} values, can be divided into the following four groups.[19] (a) $4/5 < R^{abs}/R^{em} < 2$. This applies for the majority of the compounds studied: hydrindanone, 3-methylcyclopentanone, 2,2,3-trimethylcyclopentanone, 5-ketoborneol, 5-ketobornyl acetate, and 6-ketobornyl acetate. (b) $R^{abs}/R^{em} \approx 4$ for α-fenchocampherone. (c) $R^{abs}/R^{em} < -10$ for camphor and epiandrosterone. (d) $R^{abs}/R^{em} \approx -2$ for camphenilone. In arriving at the above classification use has been made of the various spectra in *n*-heptane, except for epiandrosterone which was measured in methanol only.

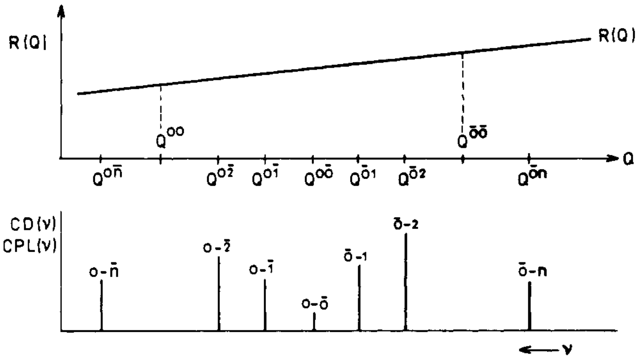


Figure 5. Correlation of the rotational strength as a function of Q and optical activity as a function of frequency.

When we assume that $R(Q)$ is a linear function of Q and that the shift of origin $Q^{\bar{o}\bar{o}} - Q^{oo}$ is equal for all compounds studied, the knowledge of R^{abs}/R^{em} allows the construction of the shapes of the functions $R(Q)$ for cases a-d. They are displayed in Figure 6, where for convenience all R^{abs} are taken equal. At the bottom of the same figure the predicted qualitative band shapes of CD and CPL are given. In case (a) $R(Q)$ invariably is positive in the entire region where the vibrational transition densities $o\bar{n}$ and $\bar{o}n$ can have nonvanishing values. Therefore no changes of sign are expected for the optical activity, neither in CD nor in CPL. In (b) the quantities R^{abs}, R^{em}, and $R(Q^{o\bar{o}})$ are all positive, but for large n the CPL curve crosses the zero line. With (c) the integrated CD is large and positive, the integrated CPL has a small negative value and the optical activity in the (o,o) band is positive, resulting in a change of sign near the central frequency of the emission curve. In case (d) the larger negative value of R^{em} as compared to (c) causes a shift of the zero point of the optical activity towards the $Q^{o\bar{o}}$ region. In the figure this results in a bisignate CPL curve but a bisignate CD could have been obtained as well, e.g., if somewhat different shapes of o and $\bar{o}$ had been taken.

From a comparison of the experimental spectra with Figure 6 it appears that the agreement of the observed and predicted band shapes is quite good. We take this as an indication that our model, notwithstanding its simplicity, is essentially correct.

4. Discussion

The discussion in the preceding section is a further elaboration of the observation made in part 3a that the large difference which exists between the values of the integrated CD (i.e., R^{abs}) and the integrated CPL (R^{em}) has to be of consequence for the CD and CPL as a function of frequency. In part 3c it is shown that it is possible to predict qualitatively the band shape of the optical activity in absorption and emission on the basis of a simple model. The success of the model in accounting for the observed phenomena not

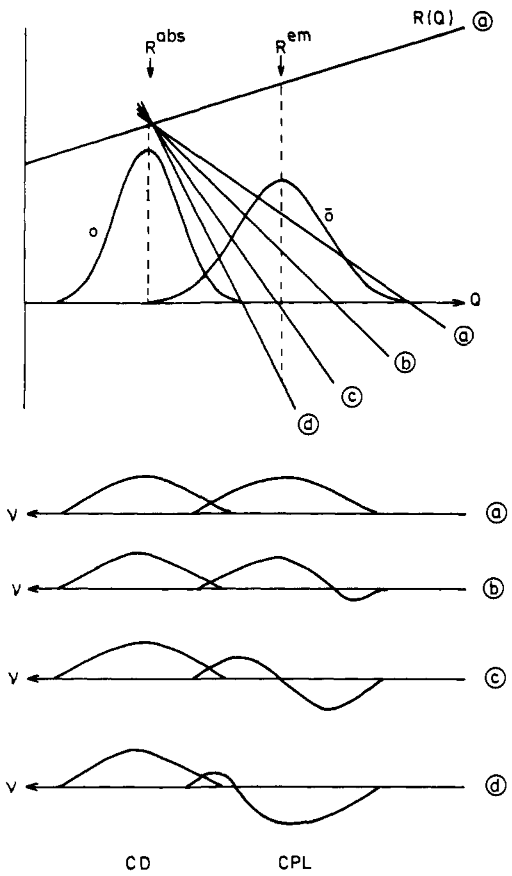


Figure 6. Top half: Zero-point-vibrational wave functions in the ground state (o) and $^1n\pi^*$ state (ō), electronic rotational strength as a function of Q for cases a-d; see text. Lower half: Corresponding band shapes of CD and CPL.

only contributes to a better understanding of bisignate Cotton effects as such, it also has some important implications.

The first pertains to the general description of the optical activity in the n-π^* transition of ketones. We find that a linear relationship of R and Q satisfactorily explains for our ketones the observed band shapes in CD and CPL. Therefore we see no reasons why higher order terms should be indispensable for the description of the lion's share of the optical activity of ketones in their n-π^* transition. This implies that probably the convenient framework of case II of Moffitt and Moscowitz is still adequate to describe the optical activity of ketones, even if they exhibit bisignate Cotton effects. We arrive at this conclusion because the first-order dependence of R on Q more likely originates in a variation of $\mathbf{r}_{\mathrm{ON}}$ with Q than in a dependence of the large magnetic dipole transition moment on the normal coordinates.

It is perhaps illuminating to discuss briefly the competition of vibrations and upper state geometry in the generation of optical activity. Of course, both factors play their part but with different success; although the value of $Q^{o\bar{n}}$ is determined by a product of vibrational wave functions, the variation with $\bar{n}$ of $Q^{o\bar{n}}$ (and thus of $R(\mathrm{Oo} \rightarrow \mathrm{N}\bar{n})$) is primarily due to the shift of origin, $Q^{oo} - Q^{\bar{o}\bar{o}}$. In a way of speaking, the difference in equilibrium geometry between lower and upper state enables the vibrations to exhibit in the experimental CD spectrum the variation of R in a certain region of Q space. Whereas thus in the CD (CPL) spectrum a large variation of R may be reflected, summation over all vibrational structure yields the rotational strength pertaining to the equilibrium configuration of the molecule in its ground (excited) state. This favorable circumstance permits one to draw a practical conclusion: in correlating a bisignate circular dichroism curve with ground state structure, in general the entire CD and not just one of the two branches has to be taken into account.

Weigang's explanation[8] of bisignate CD curves of ketones underrates the importance of the upper state's geometry. This deficiency is not present in a treatment of bisignate circular dichroism by Caldwell[20] but his theory, although rather general, is very complex. That bisignate Cotton effects can be explained from a simple linear relationship of R and Q has not been noted prior to our investigation.

So far we did not deal with the question which specific vibrations could be operative in the structuring of the CD and CPL spectra of ketones. From calculations[21] it follows that the geometry of the $^1n\pi^*$ state of formaldehyde differs from that of the ground state in two important respects. Firstly the carbonyl bond is lengthened by +0.29 Å (experimental value +0.12 Å),[22] and secondly the configuration around the carbon atom no longer is planar but pyramidal, the calculated out-of-plane angle being 32.7° (experiment, 33.6°).[22] Completely in accord with these data the n-π^* transition of formaldehyde shows long progressions in the carbonyl stretch and out-of-plane bending frequencies. These two geometry changes in the parent compound being so prominent, it is plausible that they are also present—although perhaps modified to some extent—in the low-symmetry ketones. In this respect we recall that for a proper understanding of the spectral properties of β-hydrindanone,[11] particularly, the geometry change along the normal coordinate of the carbonyl out-of-plane bending mode has to be taken into account. However, for the latter compound the energy of the upper state, as a function of the out-of-plane angle, is a double minimum potential because of symmetry reasons, but this is no longer the case for low-symmetry ketones. Here we presumably encounter for the excited state at most a skew energy curve whose minimum is either above or below the original carbonyl plane. In this connection it might be interesting to try and decide from the CD and CPL data in which direction the oxygen atom moves upon excitation. Using models which correlate rotational strength with structure, we are in the process of doing this.[7] Furthermore, from high resolution measurements on ketones, at low temperatures or in the gas phase, we hope to obtain more detailed information on vibronic rotational strengths which, hopefully, will provide us with the means for a more exacting comparison of theory and experiment. Perhaps at that stage it will be possible also to make more pertinent statements about the nature of the active modes which are involved in the vibronic optical activity of ketones.

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Thione Photochemistry. Cycloaddition in a Saturated Alicyclic System[1,2]

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Abstract: Irradiation of adamantanethione (λ 500 nm) gives the dimer, a 1,3-dithietane. In the presence of olefins thietanes are obtained in a regiospecific, nonstereospecific reaction. The regiospecificity is that expected with the formation of the more stable possible biradical intermediate. In one case, that of α-methylstyrene, support for the intermediacy of the biradical comes from the isolation of an "ene" product and proof that the latter is formed by intramolecular hydrogen transfer. It is shown that the reactive state of the thione is $^3(n,\pi^*)$ and that $\Phi_{isc} \sim 1$. Rate constants for dimerization and the addition to ethyl vinyl ether and acrylonitrile have been obtained, and the inefficiency in dimerization and cycloaddition ($\Phi \sim 10^{-4}$) shown to be due to reversion in an intermediate or intermediates to regenerate starting material, and not to a slow reaction. In the case of dimerization, trapping of the thione triplet by thione is diffusion controlled. The mechanism of addition is discussed and the intervention of complexes suggested.

After a long lapse of time, interest has begun to be drawn toward the photochemistry of the thione grouping. While studies in carbonyl photochemistry were initiated at the turn of the century and continue with vigor unabated, similar thione studies date only from the past decade.[3-13] With the exception of a single report on the reduction of adamantanethione[14] all mechanistic studies have been concerned with aromatic compounds. In fact, when the present work was initiated[15] there were no reports of the photochemical behavior of a normal saturated thione, and the position has, essentially, remained unchanged.[16]

One of the interesting features that has emerged in the study of aromatic thiones is that they have, under certain circumstances, the capacity to react from both higher and lower excited states, and evidence for this has been forthcoming from reactions as diverse as reduction, cycloaddition, and cyclization.[3,4,7,9b,12,13,17] This behavior may well, in part, be attributed to the longer lifetime of the S_2 state which is, itself, partly a consequence of the large S_1–S_2 energy separation.[18] The separation in aliphatic thiones is rather similar, and it is the purpose of this and a following paper in this series to show that a like situation obtains in the photochemistry of a typical alicyclic thione, adamantanethione (**1**). In the present paper we record the first cycloaddition reactions of an alicyclic thione and present a detailed study of the consequences of excitation into the n,π* state; in that to follow we will describe the different consequences of excitation into the S_2 state.

Results

Adamantanethione,[19] a typical saturated thione, shows four bands in the absorption spectrum between 200 and 500 nm. These are, in increasing energy, $S_0 \rightarrow T_1$, $S_0 \rightarrow S_1$ (n,π^*), $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$ $(\pi,\pi^*,\ n,\sigma^*)$.[20] No fluorescence has been detected and the S_1 and S_2 energies can only be approximated from the absorption spectrum. Values (nonpolar solvent) of near 56 and 95 kcal/mol seem probable. The triplet energy, based on the emission from a glassy matrix at 77 K[20a] and from the absorption spectrum, is near 52.6 kcal/mol.

Reactions and Products

(a) **Photodimerization.** Irradiation of **1** in benzene, λ >420 nm, gave the dimer, **2** (Scheme I). The structure of the latter followed from the molecular weight (358 by osmometry, molecular ion 332, and strong accompanying peak at 166), the NMR spectrum, and its conversion to adamantane by Raney nickel reduction. It was identical in all respects with material made by Greidanus by the acid treatment of the thione.[19] The photochemical reaction could be sensitized with benzophenone.

(b) **Cycloaddition to 1,1-Diphenylethylene, Ethyl Vinyl Ether** (E), **and Acrylonitrile** (A). A benzene solution of **1** in the presence of the olefins named gave a single product together with the dimer **2**. These were shown to have the gross structure **3**, **4**, and **5** from their composition and spectro-