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# Direct Investigation of the Validity of Vertical Approximation in the Calculation of Transition Moment Matrix Elements: n → $\pi$* Transition in Methyl Formate

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The absolute optical oscillator strength for the n → $\pi$* transition in methyl formate is calculated, within a procedure that has recently been used by our group to determine the optical oscillator strength of symmetry-forbidden transitions and which consists of expanding the (squared) transition moment along the normal coordinates of vibration. In the present work, we extend its application to a symmetry-allowed transition and discuss the applicability of the vertical approximation. To validate the present results, the UV photoabsorption cross-section was measured, and the result is compared with the one previously reported.

## I. Introduction

Esters are largely used as reagents during the manufacture of perfumes and food flavoring and are also employed as industrial solvents.[1] Despite its importance, little attention has been paid to the photochemistry of this class of compounds. New theoretical and experimental insights would be desirable in order to improve the current knowledge on the weak n → $\pi$* transition for model compounds such as methyl formate.[2,3] As far as we are aware, there is only one experimental study recently published for UV photoabsorption cross-sections of formates.[4] However, there is not any theoretical study for comparing and validating these experimental studies.

The intensity of n → $\pi$* transition in carbonylate compounds has been the subject of theoretical study by our group. The specific systems studied were formaldehyde[5] and acetone.[6] An interesting and challenging feature of the n → $\pi$* transition in $C_{2v}$ molecules such as formaldehyde and acetone is that it is symmetry-forbidden, occurring because of vibronic coupling with allowed states. In the case of methyl formate, the transition is not forbidden anymore, and as a consequence, the vertical term should furnish the major contribution to the total intensity. When an ab initio or semiempirical calculation is performed in a dipole symmetry-allowed transition, it is supposed that the terms that arise from the nonvertical contribution should be unimportant. Although this assumption can be true in some cases, there is no reason for it to be assumed as a general rule, especially when the vertical term, despite being allowed, is weak. In these cases, the other terms can play a significant part in the total intensity of the band.

The aim of the present work is to calculate the optical oscillator strength for n → $\pi$* methyl formate using molecular ab initio method, with electronic correlation taken into account by the configuration interaction (CI) technique. This property will be evaluated and discussed regarding its static (or vertical) and dynamical (or nonvertical) contributions. The experimental UV photoabsorption cross-sections previously reported[4] will be converted to optical oscillator strengths for comparison to our theoretical result.

## II. Details of the Calculation

The theoretical procedure used in the present calculations was discussed in detail elsewhere.[5] We give here only the final expression for the total optical oscillator strength for the excitation from the ground vibronic state to the sum of the vibronic states of the $\pi$* excited electronic state, expanded along the normal mode of vibration of the ground state:

$$f_{0\to k} = \frac{2}{3}\Delta E g_k[|M(0)|^2 + \sum_L \langle \xi_L(Q_L)|M_L{}^2(Q_L)|\xi_l(Q_L)\rangle] \quad (1)$$

with

$$M_L{}^2(Q_L) = \sum_j a_j\,(Q_L)^j \quad (2)$$

where, in eqs 1 and 2, $Q_L$ and $\xi_L(Q_L)$ are respectively the coordinate and the harmonic oscillator eigenfunction of the $L$th individual normal mode of vibration and $k$ refers to the electronic excited state.

$|M(0)|^2$ is the transition moment for equilibrium position. This term vanishes for a dipole forbidden transition but is expected to dominate for allowed transitions. The vertical approximation neglects the $M_L{}^2(Q_L) = \sum_j a_j(Q_L)^j$ expansion in eq 1. When this happens, the transition moment does not depend on the normal, and the expression for the total optical oscillator strength in the vertical approximation becomes simply

$$f(E)_{0\to k} = \frac{2}{3}\Delta E g_k |M(0)|^2 \quad (3)$$

where there is not any dependence on the vibration wave functions.

The expansion coefficients $a_j$ in expression 2, for each $L$ normal mode, are determined by directly calculating $M_L{}^2(Q_L)$ for some $Q_L$ values. The electronic wave functions for the different $Q_L$ values are determined through the configuration interaction method.

## III. Results and Discussions

The geometry was optimized and the vibrational frequencies were calculated in a MP2/6-311G** level. For the calculation

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**TABLE 1: Calculated Compared to Experimental Vibration Frequencies of the Ground State**[a]

| number (symmetry) | approximate type of mode[b] | our calculated frequencies ($cm^{-1}$) | experimental frequencies ($cm^{-1}$) Shimanouchi[8] | | comparison (%) |
|---|---|---|---|---|---|
| | | | value | uncertainty | |
| $\nu_1$ (a′) | $CH_3$ d- stretch | 3065 out | 3045 | 6~15 | 0.66 |
| $\nu_2$ (a′) | $CH_3$ s- stretch | 2948 out | 2969 | 6~15 | 0.71 |
| $\nu_3$ (a′) | CH stretch | 2941 | 2943 | 6~15 | 0.07 |
| $\nu_4$ (a′) | C=O stretch | 1713 out | 1754 | 3~6 | 2.34 |
| $\nu_5$ (a′) | $CH_3$ d-deform | 1450 | 1454 | 6~15 | 0.28 |
| $\nu_6$ (a′) | $CH_3$ s- deform | 1438 | 1445 | 6~15 | 0.48 |
| $\nu_7$ (a′) | CH bend | 1351 out | 1371 | 6~15 | 1.46 |
| $\nu_8$ (a′) | C−O stretch | 1192 out | 1207 | 3~6 | 1.24 |
| $\nu_9$ (a′) | $CH_3$ rock | 1140 out | 1166 | 6~15 | 2.23 |
| $\nu_{10}$ (a′) | O−$CH_3$ stretch | 923 | 925 | 3~6 | 0.22 |
| $\nu_{11}$ (a′) | OCO deform | 743 out | 767 | 3~6 | 3.13 |
| $\nu_{12}$ (a′) | COC deform | 301 out | 318 | 6~15 | 5.35 |
| $\nu_{13}$ (a) | $CH_3$ d- stretch | 3027 | 3012 | 6~15 | 0.50 |
| $\nu_{14}$ (a) | $CH_3$ d- deform | 1421 | 1443 | 15~30 | 1.52 |
| $\nu_{15}$ (a) | $CH_3$ rock | 1144 out | 1168 | 6~15 | 2.05 |
| $\nu_{16}$ (a) | CH bend | 1001 out | 1032 | 3~6 | 3.00 |
| $\nu_{17}$ (a) | C−O torsion | 331 | 332 | 6~15 | 0.30 |
| $\nu_{18}$ (a) | $CH_3$ torsion | 150 out | 130 | 6~15 | 15.38 |

[a] The calculated frequencies were scaled by a factor of 0.9496.[7] [b] d means degenerate, and s means symmetric. Out means that the value is slightly out of uncertainty range.

**TABLE 2: Per-Mode Contribution to the Total Optical Oscillator Strength ($10^{-3}$) for n → $\pi$* in Methyl Formate**

| contribution | | theory: present result | experiment: present result | experiment: ref 4 |
|---|---|---|---|---|
| vertical[a] | | 1.08 | | |
| nonvertical[b] | $Q_1$ | $7 \times 10^{-4}$ | | |
| | $Q_2$ | $3 \times 10^{-2}$ | | |
| | $Q_3$ | $3 \times 10^{-3}$ | | |
| | $Q_4$ | $3 \times 10^{-2}$ | | |
| | $Q_5$ | $8 \times 10^{-3}$ | | |
| | $Q_6$ | $4 \times 10^{-2}$ | | |
| | $Q_7$ | $3 \times 10^{-2}$ | | |
| | $Q_8$ | $-2 \times 10^{-3}$ | | |
| | $Q_9$ | $1 \times 10^{-3}$ | | |
| | $Q_{10}$ | $3 \times 10^{-2}$ | | |
| | $Q_{11}$ | $2 \times 10^{-2}$ | | |
| | $Q_{12}$ | $8 \times 10^{-2}$ | | |
| | $Q_{13}$ | $2 \times 10^{-4}$ | | |
| | $Q_{14}$ | $2 \times 10^{-2}$ | | |
| | $Q_{15}$ | $-5 \times 10^{-6}$ | | |
| | $Q_{16}$ | $3.4 \times 10^{-1}$ | | |
| | $Q_{17}$ | $-2 \times 10^{-2}$ | | |
| | $Q_{18}$ | $4 \times 10^{-2}$ | | |
| total | | 1.73 | 1.78 | 1.54 |

[a] First term in the right-hand side of expression 2. [b] Second terms in the right-hand side of expression 2.

of the transition moments (oscillator strengths), the MRCI/6-311+G** level of calculation was used. The frequencies were scaled using a factor of 0.9496[7] to compute the optical oscillator strengths by means of eq 1 above. They are presented in Table 1 and are compared to experimental frequencies.[8] This table shows that the general agreement between theory and experiments is excellent, with most of the frequencies slightly underpredict the experimental values by only <3%, except for modes 12 and 18, which differ by 5% and 15%, respectively, from the experimental results.

The calculated optical oscillator strength is presented in Table 2 as well as the experimental results. The latter was obtained by the measured UV photoabsorption cross-sections of Vésine and Mellouki.[4] So as to confirm this last result, one of us (A.S.P.) measured the UV photoabsorption cross-section for the same transition at NCAR using the apparatus described by Staffelbach et al.[9] Figure 1 compares these results, showing a good general agreement between the two sets of experiments.

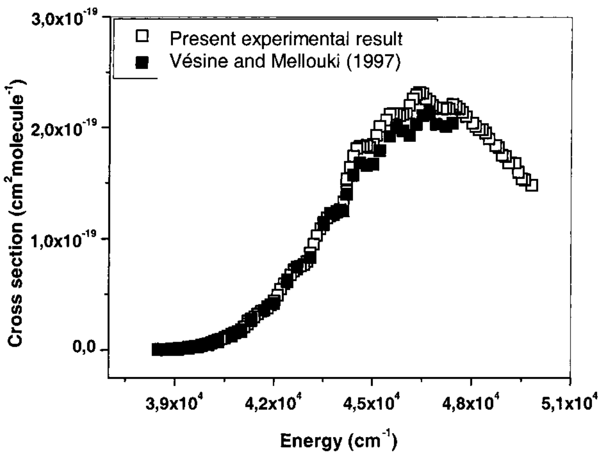

**Figure 1.** Measured cross-section for transition in methyl formate.

The small differences on the top of the absorption band in Figure 1 are responsible for the observed differences in the experimental results for the total optical oscillator strength of about 15%. The cross-section for energies higher than $5.0 \times 10^4$ $cm^{-1}$ were extrapolated by assuming a Gaussian shape to get the total integrated strength. Our theoretical result agrees very well with the experimental result measured here and differs by only about 15% from the experimental results of Vésine and Mellouki, an outstanding agreement considering the deviations commonly found in this kind of experiment.

Considering now the calculated optical oscillator strengths, it is seen that the vertical approximation cannot, quantitatively, account for the total intensity. The contribution of nonvertical terms being about 37% of the total intensity is clearly significant, and as stated above, the dynamic terms, meaning terms that depend on the normal coordinates, should not always be neglected, as is common practice in calculations involving transition moment matrix elements. The normal mode related to the CH bend ($Q_{16}$) has the largest nonvertical contribution to the calculated optical oscillator strengths. It is seen that other normal modes also contribute considerably to that property because of a possible distribution of electronic density along the methyl formate. Thus, the normal modes of molecule groups such as $CH_3$, which would not influence a priori the n → $\pi$* transition in methyl formate, have a considerable contribution. An interesting feature is that there are some modes which contribute to decrease the total intensity of the band (C−O stretch $Q_8$, $CH_3$ rock $Q_{15}$, and C−O torsion $Q_{17}$). The $CH_3$ rock ($Q_{15}$) contribution is negligible. Nevertheless, the C−O stretch ($Q_8$) and C−O torsion ($Q_{17}$) are not negligible, especially the last one.

## IV. Conclusion

We have investigated the contribution of non-Franck−Condon terms in the total intensity of the n → $\pi^*$ transition in methyl formate and found that the nonvertical terms represent 37% of the total optical oscillator strength and cannot be omitted in a quantitative study. The results were confirmed by experimental determination of the total optical oscillator strength for the same transition, with an excellent agreement between the theoretical and experimental results for the OOS. It is worth mentioning that the study of nonvertical contributions to the absolute optical oscillator strength is relatively common for diatomic molecules[10−12] but still rare for polyatomic molecules.

From the analysis of per-mode contribution above, one can verify that the validity of the vertical approximation, in general, can hold in two cases. First, the nonvertical terms are negligible when compared to the vertical one. Second, the nonvertical terms may cancel one another, because some of them increase whereas others decrease the total intensity of transition. This is clearly not the case for the weak n → $\pi^*$ transition in methyl formate, as we have shown in the present work.

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