Theoretical Investigations on Valence Vibronic Transitions

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This article reviews previously employed methods to study several valence electronic transitions, optically forbidden or not, enhancing intensity through vibronic coupling. Electronic transition dipole moments were calculated using several ab initio methods including electron correlation. In this method the square of the electronic transition dipole moments are directly calculated along the normal coordinates of vibration and then expanded with a polynomial function. Afterwards, analytical vibrational integration using harmonic wave functions, of the square of the transition moments function, allows us to obtain partial (i.e. for each vibrational mode) and total optical oscillator strengths (OOS), for the vibronic transition of interest. We illustrate the accuracy of the method through valence transitions of benzene (C_6H_6), formaldehyde (H_2CO), acetone (C_3H_6O) and formic acid (HCOOH).

I. INTRODUCTION

Absolute intensities of excitation processes, either through photon absorption or electron impact, have been calculated for a long time. At the beginning of these type of calculations, empirical wave functions were used while nowadays the more accurate ab initio methods are employed. The great majority of these works used the Born-Oppenheimer approximation, that is, the separation of the electronic, vibrational and rotational wave functions at the equilibrium geometry. This approach is very accurate when the separation between the electronic and the vibrational motions is well established. In the opposite situation, when the coupling between the electronic and the vibrational motions (i.e., the vibronic coupling) is strong, this procedure fails. In other words, since molecules are constantly vibrating, they may undergo geometry distortions that induce electronic-vibrational transitions otherwise symmetry forbidden. In these cases the oscillator strengths have contributions from molecular vibration, and the dynamics of nuclei may change the selection rules through the coupling between the electronic and nuclear movements. These changes in selection rules are particularly important for certain transitions that although being dipole forbidden, appear with considerable intensity in the optical spectrum.

Vibronic coupling is also relevant to the rate of radiationless internal conversion of one electronic state to another, both with the same multiplicity. Internal conversion (IC) is quite common in photochemistry: many photodissociation reactions proceed through IC from the excited to the ground state potential energy surface. Although the method we present here does not allow the complete calculation of rate constants of IC processes, we still can draw conclusions concerning it, as will be shown in the study of formic acid. The knowledge of the vibronic effects involved in IC effects is crucial for understanding photodissociation mechanisms and dynamics [1, 2].

The theory of vibronic coupling and intensity of symmetry-forbidden transitions [3] have been established long ago by Herzberg and Teller [4]. They have set the principles that control which normal vibrations make a transition allowed, and how to calculate band intensities from the knowledge of the molecular electronic wave functions in its equilibrium nuclear configuration. The Herzberg-Teller theory employs a first-order perturbation expansion in the usual way of quantum mechanics [5].

Although a general theory of vibronic coupling is now well established [2], practical calculations based on ab initio wave functions are scarce. Most of the previous studies concerned formaldehyde and benzene. Murrell and Pople [6] applied the Herzberg-Teller theory to the $^1B_{2u}$ and $^1B_{1u}$ transitions in benzene to obtain relative intensities. Shortly afterwards, in 1957, Pople and Sidman [7] applied the perturbation expansion to study the optically forbidden electronic transition $A_2 \leftarrow A_1$ in the H_2CO molecule. Other related works are discussed in the results and discussion section.

In most of the published works, the closure relation was used to sum all the final vibrational states of the final electronic state along with perturbation theory to take into account the vibronic coupling between the different electronic states. Other theoretical calculations followed, considering the vibronic coupling through perturbation theory and using sum rules to account for all the vibrational states of a particular electronic state or to obtain individual vibronic intensities [2].

The closure relation has also been extensively used for other purposes by spectroscopists [8–12]. Among its applications, the closure relation was used to normalize the experimental electron impact excitation cross sections [12], to calculate dissociation cross sections within the reflection approximation [10, 13], and to determine zero-point corrections to vertical excitation energies [11]. In several situations the experimental spectrum does not present vibronic resolution, even for small molecules. In such cases the experimental optical oscillator strengths (OOS), and the equivalent property for electron impact, the generalized oscillator strength (GOS), are deter-

mined for the whole electronic band, i.e., the sum of the vibronic levels associated with a particular electronic excitation process. These reasons contributed to the interest in applying the closure relation as in the original procedure employed by Murrel and Pople [6], as did other theoretical calculations concerning vibronic coupling [14–16] or direct electronic excitations [17, 18].

Contrary to the widespread use of the closure relation, the application of perturbation theory to describe the coupling between the different vibronic states was subject to some controversy. Orlandi and Siebrand [19] pointed out that, since this procedure considers only selected couplings, it may lead to significant errors. Ziegler and Albrecht [20] have discussed these problems in a work on Herzberg-Teller vibronic excitations of benzene. They have /*determined the OOS using a closure relation and directly calculating the electronic matrix elements along the normal coordinates and assuming a linear dependence on the coordinates. Four years later, in 1978, Van Dijk et al. [21–23] also directly calculated the electronic matrix elements along the normal coordinates for the individual vibronic bands of the $A_1 \rightarrow A_2$ electronic transition of H_2CO. They obtained the OOS fitting the electronic matrix components to a polynomial function and using the closure relation for the excited vibronic states.

A crucial step in the study of systems involving excited electronic states is the quality of the corresponding wave functions. Early attempts to study vibronic coupling, like the ones discussed above, lacked the possibility of using good quality wave functions. In our previous works reviewed here we stress the importance of the electronic wave functions.

This article reviews previously employed methods to study several electronic transitions, valence or inner-shell, optically forbidden or not, through photon absorption [24–28] and electron impact [29], enhancing intensity through vibronic coupling. We illustrate its usefulness through the valence transitions of benzene (C_6H_6) [28], formaldehyde (H_2CO) [24], acetone (C_3H_6O) [25] and formic acid (HCOOH) [30] that we have studied.

II. THEORETICAL FRAMEWORK

A. General considerations

There are some electronic transitions that, although optically forbidden due to symmetry restrictions, appear with moderate intensity in the spectrum. The reason is vibronic coupling, which was first explained by Herzberg and Teller [4, 31, 32]. In the Herzberg-Teller effect the vibrational motion and the electronic degrees of freedom can no longer be separated. In this case, the total vibronic symmetry, $\Gamma^{el} \otimes \Gamma^{vib} = \Gamma^{vibronic}$, must be examined. In the general case, in order to calculate the transition intensity and evaluate the allowed (in the vibronic sense) transitions, it is necessary to examine the transition moment integral

$$\langle \psi_{vibronic} | \mu | \psi_{vibronic} \rangle$$

where μ is the dipole function.

The intensity of the vibronic transition depends on the degree of mixing of the vibrational and electronic wave functions. Basically, there are two approaches available to calculate this intensity. One is through first-order perturbation theory [2, 31] which applies as long as this mixing is not too extensive. In this approach, the coupling is taken into account through matrix elements involving the electronic wave functions of both states and the derivative, with respect to the normal coordinates, of the Coulomb interaction potential between electrons and nuclei - this is the perturbation term to the equilibrium electronic molecular hamiltonian. The excited-state wavefuntion becomes mixed with other (or others) zeroth-order electronic state(s) through the perturbation term. In most situations the interaction is considered to take place between two electronic states. The corresponding interaction matrix between two excited states, divided by the energy separation between them, determines the magnitude of the vibronic coupling. This term is separated from the electronic transition dipole moment, which is calculated at the ground state equilibrium geometry. The second approach, the direct method, which we use, is discussed in the next section. When available, our results are compared with values obtained from perturbation theory.

B. The direct method

The direct method, with small variations, has been applied before by other authors [21–23, 33]. The starting point of the calculation is the Born-Oppenheimer approximation for the total wave function,

$$\Psi_{kv} = \psi_k(\mathbf{r}; \mathbf{Q}) \chi_{kv}(\mathbf{Q}) \tag{1}$$

where $\mathbf{r}$ represents the coordinates of the electrons and $\mathbf{Q}$ the coordinates of the nuclear vibrational normal modes. In turn, ψ_k and χ_{kv} are the electronic and vibrational wave functions for the (k, v) vibronic state.

The optical oscillator strength $f(E)_{kv \leftarrow 00}$ for excitation from the $v = 0$ vibrational level of the (ground) electronic state $k = 0$ to the v vibrational level of the k-th electronic state assumes the form

$$f(E)_{kv \leftarrow 00} = \frac{2}{3} \Delta E g_k | \langle \chi_{kv}(\mathbf{Q}) | M_{0k}(\mathbf{Q}) | \chi_{00}(\mathbf{Q}) \rangle |^2 \tag{2}$$

where ΔE is the excitation energy of the vibronic transition $kv \leftarrow 00$, g_k is the degeneracy of the final state and the electronic transition dipole moment, in atomic units, is given by

$$M_{0k}(\mathbf{Q}) = -\langle \psi_k(\mathbf{r}; \mathbf{Q}) | \sum_{i=1}^{n} r_i | \psi_0(\mathbf{r}; \mathbf{Q}) \rangle \tag{3}$$

Now we make crucial approximations in three steps. First, we sum over all discrete vibrational levels and integrate over the continuum of the k-th electronic band. Second, we replace the transition energy ΔE, corresponding to the energy difference between the vibrational levels of the two electronic states, by an average value $\bar{E}$, usually taken as the electronic energy difference, either calculated or measured. Third, after

expanding the square modulus of matrix element and using the completeness relation for the vibrational states of the final (k) state, $\sum_v |\chi_{kv}(\mathbf{Q})\rangle\langle\chi_{kv}(\mathbf{Q})| = 1$, we obtain, for the total intensity of the whole band [6], the following result:

$$
\begin{aligned}
f(E)_{k\leftarrow 0} &= \sum_v f(E)_{kv\leftarrow 00} \\
&= \frac{2}{3}\sum_v \Delta E g_k |\langle\chi_{kv}(\mathbf{Q})|M_{0k}(\mathbf{Q})|\chi_{00}(\mathbf{Q})\rangle|^2 \\
&= \frac{2}{3}\bar{E} g_k \langle\chi_{00}(\mathbf{Q})|M_{0k}^2(\mathbf{Q})|\chi_{00}(\mathbf{Q})\rangle
\end{aligned}
\tag{4}
$$

Note that in this expression only the normal modes of one of the states, usually the ground state, is involved and transitions are from the (ground) vibrational state ($v = 0$). The normal modes coordinates and the corresponding ground state frequencies, used in the calculations were obtained, in most cases, at the Moller-Plesset second-order (MP2) level.

We now assume that the total dipole transition moment is the sum of the transition dipole moments for each normal mode vibration L that contributes to the band intensity. One then gets,

$$
\begin{aligned}
M_{0k}(\mathbf{Q}) &= \sum_L M_{0k}(Q_L) \\
&= \sum_L -\langle\psi_k(\mathbf{r};Q_L)|\sum_{i=1}^n r_i|\psi_0(\mathbf{r};Q_L)\rangle
\end{aligned}
\tag{5}
$$

In turn, the nuclear wave function $|\chi_{00}\rangle$ is expressed in the framework of the harmonic approximation as

$$
|\chi_{00}(Q_1,Q_2,\ldots,Q_J)\rangle = \prod_{L=1}^J |\xi_L(Q_L)\rangle,
\tag{6}
$$

where $|\xi_L(Q_L)\rangle$ are the wave functions of each normal mode in the ground state. Combining Eq. (4) to Eq. (6), we obtain for the OOS summed over the J vibrational modes of the k-th excited state

$$
f(\bar{E}) = \frac{2}{3}\bar{E} g_k \sum_L \langle\xi_L(Q_L)|M_{0k}^2(Q_L)|\xi_L(Q_L)\rangle
\tag{7}
$$

The integral in Eq. (7) over the harmonic functions $\chi_{00}(Q_L)$ is straightforward. Calculations of $M_{0k}(Q_L)$ for the molecules studied were done with post Hartree-Fock methods, including Configuration Interaction (CI) and Complete Active Space Self Consistent Field (CASSCF) wave functions, for several multiple values of Q_L along each ground state normal mode coordinate contributing to the vibronic coupling. Afterwards, $M_{0k}^2(Q_L)$ is expanded as a power series,

$$
M_{0k}^2(Q_L) = M_{0k}^2(0) + a_1(Q_L) + a_2(Q_L)^2 + \ldots
\tag{8}
$$

where $\{a_j\}$ are numerical constants obtained through fitting of the calculated values. If the transition is optically forbidden, the first term in Eq. (8) should be zero, otherwise it will be expected to be the dominant one. For a dipole forbidden transition, the remaining expansion terms account for the transition intensity. The result of the above expansion is to simplify

the problem through the calculation of the transition dipole moment M_{0k} only along the normal coordinates, thereby limiting it to J sections of potential energy surface. The effect of the assumption, Eq. (8), is that vibronic transitions induced by correction terms to it, for instance, via crossed terms, are not taken into account. It should be noted that Eq. (7) does not employ the Franck-Condon, or vertical, approximation, that would imply the calculation of the excited state vibrational wave functions and the corresponding overlap integral with the ground state vibrational functions.

It is through the use of multiconfiguration methods for the two electronic wave functions, ψ_0 and ψ_k, calculated along each normal mode coordinate Q_L, that vibronic effects, including the effect of other excited electronic states, are taken into account. When we write the vibrational ground state wave function as a product of harmonic functions, and use the completeness for the excited state vibrational wave functions, we neglect the intermode coupling in both electronic states [22]. Besides, if we use the normal coordinates for the ground state along with the completeness for the excited state, i.e., we use only the ground state normal modes, as we have done, we neglect rotation of the normal coordinates with respect to each other, the so-called Duschinsky effect [22, 34] and anharmonic effects. The accuracy of these approximations, including the fitting of the transition dipole moment calculated along the normal coordinates, is given by the comparison between the calculated OOS per mode and the experimental results, when available. We illustrate it presenting our results in the next section.

III. RESULTS AND DISCUSSION

We now illustrate the range of applicability and the accuracy of the methodology just described through the a selection of molecules we studied.

A. Benzene, C_6H_6

Benzene is a textbook case of vibronic transitions [31, 35]. The valence transitions $1^1B_{2u} \leftarrow \tilde{X}$ and $1^1B_{1u} \leftarrow \tilde{X}$, symmetry forbidden, appear with considerable intensity in the optical spectrum due to vibronic coupling. Several theoretical studies investigated one or both transitions, using perturbation theory [6, 14, 36], and/or including the Duchinsky effect [37–40]. The older works have mostly used semiempirical wave functions, while the more recent ones employed Complete Active Space Self Consistent Field (CASSCF) electronic wave functions.

We have studied both symmetry forbidden transitions [28]. The electronic wave function used was a CASSCF(6,6)/cc-pvdz which was built from six valence π orbitals and 6 electrons, perfectly adequate to describe these $\pi \rightarrow \pi^\star$ transitions [40]. The molecular orbitals to calculate the transition dipole moments were state averaged for each transition, an approach that improves the accuracy of the transition dipole moments by providing a balanced description of each pair of

states [41]. For the ground state frequencies and optimization we have used the CASSCF(6,6)/6-31G** method. For each normal mode, the ground state CASSCF frequencies employed to compute the harmonic integrals in Eq. (7) have been scaled by 0.92. Our computed vertical transition energies for each state are 4.90 eV (B_{2u}) and 6.20 eV (B_{1u}), being used as the average energy $\bar{E}$ in Eq. (4) to obtain the oscillator strengths for each normal mode.

We first discuss the $1^1B_{2u} \leftarrow \tilde{X}$ transition. The transition dipole moments belong to the e_{1u} (x and y in-plane components) and a_{2u} (z out-of-plane component) irreducible representations (D_{6h} symmetry). Thus, this transition is optically forbidden by symmetry reasons, and hence the first term in the expansion of Eq. (8) should vanish [35]. However, through the vibrations of e_g and b_{1g} symmetries, higher-order terms will become nonzero. Since there is no b_{1g} vibration in benzene, only the in-plane e_{2g} degenerate modes ν_6, ν_7, ν_8, and ν_9 will contribute in first-order to the band intensity [40].

Some of the fits of the computed $M_{0k}^2(Q_L)$ values, for both transitions, using Eq. (8), included only up to second-order terms, and some to third-order. Note that, for the expansion of the transition dipole squared in Eq. (8), it is necessary to consider only positive values of the displacement along a normal coordinate since $M_{0k}^2(Q_L)$ is an even function [25] of the normal modes considered here.

In Table I we present the total integrated OOS and the contribution from each vibrational normal mode to the 1^1B_{2u} transition, and other available results. Although Metz *et al.* [42] claim that the inclusion of the Duchinsky effect may raise the theoretical results for this transition by about 20%, the experimental results of Fischer *et al.* [43] have not shown any marked contribution of the Duchinsky effect. We have not included this effect in our calculations.

The experimental spectra around the 4.9 eV region show more than 25 vibronic bands originated from the ν_6, ν_7, ν_8 and ν_9 inducing modes. The vibronic bands from the ν_6 inducing mode is responsible for about 90% of the total OOS, and their components $6_0^1 1_0^n$ ($n = 0 - 5$) are clearly identified in the optical spectra. The other vibronic modes, from the ν_7, ν_8 and ν_9 inducing modes, are not as easily identified in the optical spectra as the mode ν_6 and, as expected, Table I shows some discrepancy concerning the relative intensities of the experimental results. In particular, the experimental results of Callomon [44] do not report any contribution from the ν_8 mode, and the measurement of Stephenson *et al.* [45] shows a contribution of 0.6%.

Table I shows that, except for the results of Ziegler and Albrecht [20] and Metz *et al.* [42], the other theoretical and experimental results agree that the inducing ν_6 mode is responsible for about 90% of the total OOS of these vibronic bands. Nevertheless, they do not agree, in general, for the absolute values for the OOS as well as on the relative contributions of the other inducing modes (ν_7, ν_8 and ν_9).

The theoretical results presented in Table I employed different methods both in the calculations of the wave functions, used to determine the electronic matrix elements, and in the method utilized to determine the vibronic coupling. Table I shows that they can affect both the absolute values, and the relative contributions of the different inducing modes.

Among the methods that considered perturbation theory to calculate the vibronic coupling, the early results of Albrecht [20] clearly overestimates the intensities of these vibronic bands. Both Roche and Jaffé [14] and Metz *et al.* [42] used the semiempirical CNDO function, although the latter took into account a possible coupling of the electronic states by more than one vibration. Their total OOS values differ by some 20% and are larger than the experimental results. Unfortunately, Orlandi *et al.* [37] presented only relative values for the OOS. Their results seem to underestimate the ν_9 inducing mode intensity and overestimate the intensity of the ν_8 inducing mode, a trend also observed in the Metz *et al.* [42] calculations.

Ziegler and Albrecht [20] directly calculated the OOS employing a procedure similar to the one we used, and used CNDO semiempirical wave functions. Their total OOS value presented a good agreement with the other CNDO results, and also overestimates both ν_8 and ν_9 inducing modes.

The theoretical results of Bernhardsson *et al.* [40] employed a CASSCF wavefunction, similar to the one used in the present calculations. Both sets of the total OOS values are lower than the other theoretical values, the results of Bernhardsson *et al.* [40] being within the reported error bars for both sets of experimental results [46, 47] while our results are within only one of the experimental results of Pantos *et al.* [46]. While both sets of calculations roughly agree on the contributions of the ν_7 and ν_9 inducing modes, our calculations indicate a larger contribution from the ν_8 than the calculations of Bernhardsson *et al.* [40] and the measurements of Callomon [44] and Stephenson *et al.* [45].

On should bear in mind when comparing all these results that, except for the contributions of the $6_0^1 1_0^n$ ($n = 0 - 5$) for the ν_6 inducing mode, the other experimental contributions from the 1^1B_{2u} are difficult to determine. The reason is that they correspond to very low intensity vibronic bands (about $1/100$ of those bands from the 1^1E_{1u} excited state) and the ν_7, ν_8 and ν_9 inducing modes are related to more than 20 vibronic bands not easily attributed in the experimental spectrum. Therefore, we suggest new experimental measurements in order to further investigate these bands and clarify the comparisons with the theoretical results.

Concerning the $1^1B_{1u} \leftarrow \tilde{X}$ transition, its theoretical study is more complicated than the previous one since the B_{1u} state is the second valence one, its surface is flat and distorted [40], and other modes contribute to the band intensity. The direct products of the irreducible representations $b_{1u} \otimes e_{1u} \otimes a_{1g} = e_{2g}$ and $b_{1u} \otimes a_{2u} \otimes a_{1g} = b_{2g}$ show that in addition to the e_{2g} normal mode one should include for this transition also the b_{2g} modes.

The total OOS value for the 1^1B_{1u} is experimentally easier to determine than for the 1^1B_{2u}, because it is about 10 times more intense. In fact, the experimental results of Pantos *et al.* [46] and Brith *et al.* [48] are in good agreement. Unfortunately, the same is not true with respect to the relative contribution of the different inducing modes. The spectrum in this region presents an ambiguous vibronic attribution [47]. Therefore, the measured contributions of the inducing modes

TABLE I: Integrated optical oscillator strengths divided by 10^{-4} ($f/10^{-4}$) for the transition $1^1B_{2u} \leftarrow \tilde{X}$ in benzene. The contributions from each inducing mode are also given. Normalized values are indicated in brackets.

Mode	Theoretical[a]					Experimental			
	this work	Ref. [42]	Ref. [37]	Ref. [40]	Ref. [20]	Ref. [45]	Ref. [44]	Ref. [46]	Ref. [47]
ν_6	3.348 (100.0)	5.9 (100.0)	(100.0)	(100.0)	4.98 (100.0)	(100.0)	(100.0)	4.7 ± 0.94	6.48
ν_7	0.1222 (3.7)		(3.0)	(5.8)	0.08 (1.7)	(3.6)	(5.9)		
ν_8	0.1341 (4.0)	1.38 (23)	(5.8)	(0.4)	2.48 (49.8)	(0.6)	$\cdots$		
ν_9	0.1965 (3.6)		(0.3)	(4.0)	0.4 (8.3)	(1.8)	(2.3)		
Total	3.80	7.28		5.35	7.94				

[a] Other theoretical results: Roche e Jaffé [14] reported 9.0×10^{-4} while Albrecht [36] calculated 60.0×10^{-4}.

should be considered only as indicative.

Table II reports the computed OOS integrated results. Except for the theoretical results of Roche and Jaffé [14], all the other calculations presented OOS values in fair agreement with the experimental results. The calculations of Roche and Jaffé [14], that employed perturbation theory to account for the vibronic coupling and CNDO semiempirical wave functions, strongly disagree with other experimental and theoretical results.

Table II shows that our results and the theoretical results of Ziegler and Albrecht [20] do not agree on the relative contributions of the inducing modes. Despite the fact that Ziegler and Albrecht [20] employed the CNDO semiempirical wave function and the present work considered the *ab initio* CASSCF method, both sets of calculations predicted similar total OOS values for these transition.

When we compare our results and those of Bernhardsson *et al.* [40] in Table II which also employed *ab initio* CASSCF wave functions, we see that both calculations agree that the major contribution comes from the ν_9 induced mode followed by the ν_8 mode. On the other hand, we estimate a lower contribution to the vibronic bands coming from the ν_6 than did Bernhardsson *et al.* [40] . Concerning this transition, contrary to the other one, the present results for the total OOS show a better agreement with the experimental results [46, 48] than those of Bernhardsson *et al.* [40] .

It is interesting to observe that the older theoretical result of Ziegler and Albrecht [20] and Roche and Jaffé [14], both with CNDO wave functions, as well as the experimental measurements, assign the largest contribution to the ν_8 normal mode, followed by the ν_6 mode. The present results and the other CASSCF [40] calculations clearly indicate that the main contribution comes from the ν_9 inducing mode followed by ν_8. These results claim a new experimental analysis.

B. Formaldehyde, H_2CO

Formaldehyde is another system for which vibronic coupling has been subject of several studies [7, 15, 15, 21, 22, 24, 49]. The H_2CO molecule is planar in the ground state, and the $A_2 \leftarrow A_1$ electronic transition corresponds to moving an electron from the highest molecular occupied orbital, $2b_2$, to the first unoccupied orbital, $1b_1$. This transition appears in the valence optical spectrum around 4 eV [50–52], and for long has been attributed to vibronic effects [7, 32].

The H_2CO molecule has six vibrational modes: three of them of the a_1 representation do not contribute to vibronic coupling, while two of b_2 (in-plane C-H antisymmetric stretching and bending) and one of b_1 (out-of-plane bending) representations do contribute. We calculated [24] the OOS using the method presented in last section for the active modes.

The electronic wave functions for the ground and excited electronic states, at the equilibrium geometries and the distorted geometries along the normal modes, were calculated with the single and double multireference configuration interaction method (MRCI). The molecular orbitals were expanded in a gaussian basis set (10s,6p,1d)/[10s,4p,1d] for carbon and oxygen and a (5s,1p)/[3s,1p] basis for the hydrogens atoms previously used [18, 53]. The virtual space was built from the 24 low-lying virtual orbitals.

Table III shows our theoretical results for each normal mode and the total OOS and the comparison with previous theoretical and experimental results. Only the present results and those of Van Dijk et al. [21–23] and Kemper et al. [23] directly calculated the electronic transition dipole moments. The other theoretical work treats the vibronic coupling via perturbation theory. Table III shows that vibronic coupling perturbation theory is not able to take into account the inducing in-plane modes Q_5 (antisymmetric stretching) and Q_6 (antisymmetric bending) of b_2 symmetry, thereby strongly underestimating the corresponding contributions to the total OOS. This situation prevails even with the modified methodology used by Roche and Jaffé [14] and Johnson [15] that included corrections due to the rearrangement of the electronic cloud, usually

TABLE II: Integrated OOS divided by 10^{-4} ($f/10^{-4}$) for the transition $1\,^1B_{1u} \leftarrow \tilde{X}$ in benzene. The contributions from each inducing mode are also given. In brackets are the normalized quantities. Except for Ref. [48], the other results are from theoretical calculations.

Mode	this work	Ref. [40]	Ref. [20]	Ref. [14]	Ref. [48](exp.)	Ref. [46](exp.)
ν_4 (b_{2g})	9.863 (1.3)	$\cdots$	0.6	10	0	
ν_5 (b_{2g})	8.137 (1.1)	(2.6)	$\cdots$	$\cdots$	0	
ν_6 (e_{2g})	14.33 (1.9)	(8.1)	162.8	150	190	
ν_7 (e_{2g})	9.838 (1.3)	$\cdots$	6.6	0.0	0	
ν_8 (e_{2g})	239.9 (31.8)	(30.0)	681.6	2000	750	
ν_9 (e_{2g})	754.0 (100.0)	(100.0)	58.8	100	0	
Total	1036	760	910	2300	940 ± 94	900 ± 180.0

not taken into account in the perturbation approach to vibronic coupling [2].

The direct method used by van Dijk et al. [21, 22] and Kemper et al. [23] presents a ratio between the induced modes consistent with the experimental results of Strickler and Barnhart [51] as well with the present results. On the other hand, the van Dijk et al. [21–23] absolute OOS (i.e., the integrated results) are more than a order of magnitude higher than our results and the experimental results. We try to rationalize this unexpected difference in the following way: although these authors used CI wave functions, they used a double zeta gaussian basis set without polarization functions on the carbon and oxygen atoms, an approach that could generate inaccurate molecular orbitals for the CI, with consequences for the OOS values calculated from them.

Table III shows that the agreement between our OOS results and the experimental values is quite good, both for the total OOS and the separate contributions originating from each normal mode. Note that the contribution due to the Q_4 mode (out-of-plane bending) is far the greatest, even though the contributions from the modes Q_5 are not negligible.

C. Acetone, C_3H_6O

The absorption spectrum of the acetone molecule, C_3H_6O, in the near ultraviolet has been studied for long [32, 54–58]. The first singlet electronic transition $A_2 \leftarrow A_1$ corresponds to an excitation $n \rightarrow \pi^\star$, the same type of transition studied for the formaldehyde, H_2CO, discussed in the last section. This transition is also symmetry forbidden but through vibronic coupling it gains intensity and appears in the spectrum.

The ground state geometry was optimized and the corresponding vibrational frequencies obtained at the MP2/6-311G** level. The electronic dipole transition moments, necessary to obtain the OOS, were calculated with the multireference configuration interaction MRCI/6-311+G** method. A total of 72821 configurations were used for the MRCI [25], which used molecular orbitals constructed with the modified virtual orbital (MVO) approach [59]. The vertical energy thus

obtained for the $n \rightarrow \pi^\star$ transition was 4.43 eV, the harmonic frequencies were scaled by 0.9496 [60], values used for the OOS calculation. Since $M_{0k}^2(Q_L)$ is a even function, we can perform the vibrational integration over positive values of Q_L and multiply the result by two.

Table IV reports our OOS values, the theoretical values of Liao et al. [58], both separated for each normal mode, and experimental results for the total OOS [54, 56]. Concerning the total OOS, our result, Liao et al.'s [58] calculation and the two experimental values [58] agree quite well despite the low absolute values. On the other hand, our distribution over the normal modes and Liao et al.'s, are quite distinct. Liao et al. obtained that 94% of the total OOS are due to b_1 symmetry inducing modes, the remaining contribution being caused by b_2 modes. According to them, the a_2 modes have a negligible contribution. Our results show that b_1 is the dominant mode, but with a smaller contribution of 66.3% to the total oscillator strength. Other contribution is 6.8% for the b_2 modes, which agrees quite well Liao et al.'s results. The major difference comes from the a_2 modes, which according to us have a weight of 26.9% on the total OOS while for them this mode almost does not contribute. Both theoretical results agree that CO out of plane wagging mode is the most effective one to borrow intensity.

The disagreement between our results and Liao et al's, the former based on the perturbation theory, concerning the mode distribution contributing to the total OOS also happened with the formaldehyde molecule [24], discussed in the last section. Concerning formaldehyde, there are available experimental results [51] separating contributions from each mode to the total OOS, that favored our calculations over the perturbation method in the Herzberg-Teller framework. The latter tends to overestimate certain modes and underestimates others while the present direct method shows a much better agreement with the experimental distribution - see Table III. Experimental results on this transition, with mode contribution separation like in formaldehyde, would be very interesting for the comparison between the two theoretical approaches.

TABLE III: Contribution per vibrational mode to the OOS ($\times 10^{-3}$) for the $^1A_2 \leftarrow X^1A_1$ electronic transition in formaldehyde. Q_4, Q_5 and Q_6 are inducing modes.

References	$Q_4(b_1)$	$Q_5(b_2)$	$Q_6(b_2)$	Total OOS
Theory				
[7]	0.3	$\cong 10^{-4}$	$\cong 10^{-4}$	0.3
[14]	0.13	6×10^{-3}	0	0.13
[15]	0.17	10^{-3}	1.2×10^{-4}	0.17
[71]	0.51	10^{-3}	0.66	1.17
[72]				0.29
[16]	0.053	$\cong 10^{-3}$	$\cong 10^{-3}$	0.053
[21]	4.62	3.06	0.87	8.55
[33]	2.27	0.74	0.19	3.20
Present results	0.143	0.040	0.024	0.21
Experiments				
[50]				0.24
[52]				0.2
[73]				0.3
[51]	0.158	0.062	0.020	0.24

TABLE IV: Optical oscillator strength values (OOS) values (this work), theoretical values of Liao et al. [58], both separated for each normal mode, and experimental results for the total OOS [54, 56] in acetone

Mode	OOS (present)	%(present)	OOS(teo) [58]	OOS(exp) [54]	OOS(exp) [56]
$Q_2(a_2)$	7.60×10^{-5}	22.36	3.5×10^{-7}		
$Q_{10}(a_2)$	1.50×10^{-6}	0.31	1.71×10^{-8}		
$Q_{11}(a_2)$	1.41×10^{-5}	4.15	2.75×10^{-9}		
$Q_{12}(a_2)$	3.96×10^{-7}	0.09	7.81×10^{-8}		
$Q_{13}(b_2)$	2.01×10^{-6}	0.59	1.10×10^{-7}		
$Q_{14}(b_2)$	5.27×10^6	1.55	2.73×10^{-6}		
$Q_{15})(b_2)$	1.33×10^{-6}	0.39	2.00×10^{-7}		
$Q_{16}(b_2)$	8.74×10^{-6}	2.57	6.32×10^{-7}		
$Q_{17}(b_2)$	$3.94 \times 10^{(-6)}$	1.16	6.39×10^{-7}		
$Q_{18}(b_2)$	3.74×10^{-4}	0.11	5.99×10^{-7}		
$Q_{19}(b_2)$	1.46×10^{-6}	0.43	1.77×10^{-5}		
$Q_{20}(b_1)$	1.07×10^{-5}	3.15	1.58×10^{-5}		
$Q_{21}(b_1)$	1.53×10^{-9}	0.00045	9.55×10^{-7}		
$Q_{22}(b_1)$	5.67×10^{-5}	16.67	8.78×10^{-5}		
$Q_{23}(b_1)$	1.43×10^{-4}	42.10	1.82×10^{-4}		
$Q_{24}(b_1)$	1.49×10^{-5}	4.37	5.26×10^{-5}		
Total	3.40×10^{-4}	100	3.62×10^{-4}	4×10^{-4}	4.16×10^{-4}

D. Formic acid, HCOOH

Formic acid, HCOOH, is an important intermediate in the oxidation of unsaturated hydrocarbons in combustion, one of the most abundant pollutants in the atmosphere, and was identified in interstellar clouds [61, 62]. Absorption of a photon of 248 nm (4.99 eV) excites HCOOH from the ground (S_0) to the first excited (S_1) electronic state ($A'' \leftarrow A'$). This transition is a n → π* taking place in the carbonyl moiety [63]. After the transition, the molecule dissociates into two main channels, $CO + H_2O$ (1) and $CO_2 + H_2$ (2). At this wavelength, dissociation on the S_1 surface, intersystem crossing, or funneling through a S_0/S_1 conical intersections to the ground state are all energetically inaccessible [64]. Therefore, it was put forward recently [62, 64, 65] that formic acid vibrationally re-

laxes from the S_1 to the S_0 state via internal conversion and/or fluorescence. Vibronic coupling can enhance the fluorescence probability (i.e, its optical oscillator strength), as we have shown above for other cases, and is responsible for the internal conversion process [2, 31]. In particular, since formic acid is planar in the S_0 state and pyramidal in the S_1 state, it can be expected a priori, due to geometrical distortion, considerable vibronic effects for the transition. Ng and Bell measured the absorption spectrum [63] and, by analogy with n → π* transitions in formaldehyde and formyl fluoride, suggested that C=O stretching (mode v_3) and CH bending (v_8, also from mode v_4), should be in the spectrum with considerable contribution. We present results for the trans-HCOOH [30] since it is the most stable conformer, the only one with measured spectrum and because our classical trajectory calculations for

TABLE V: Optical oscillator strengths (OOS) for the $S_1 \leftarrow S_0$ transition including vibronic contributions per mode, their summed contribution and total OOS which includes equilibrium geometry plus Q-dependent terms (i.e. vibronic contributions) in formic acid

Normal Mode	OOS[a]	OOS/normalized	Mode type
Eq. geometry contribution	1.14×10^{-3}		
ν_1	8.90×10^{-7}	0.00	OH stretching
ν_2	5.98×10^{-6}	0.024	CH stretching
ν_3	2.04×10^{-4}	0.82	C=O stretching
ν_4	5.16×10^{-5}	0.21	CH rock
ν_5	3.10×10^{-6}	0.012	OH bending
ν_6	3.08×10^{-5}	0.12	C-O stretching
ν_7	-4.58×10^{-6}	-0.018	OCO deformation
ν_8	2.49×10^{-4}	1.00	CH wagging out-of-plane
ν_9	-3.21×10^{-5}	-0.13	torsion
Q-dependent contribution	0.508×10^{-3}		
Total OOS (eq. value + Q-dep. terms)	1.65×10^{-3}		

[a] contribution per mode

both dissociations [66] show that the branching ratios of the two reactions are quite similar for both conformers (i.e., the trans and the cis ones).

We calculated the optical oscillator strength arising from the vertical transition and the contributions from each normal mode due the vibronic coupling [66] - results are shown in Table V. The ground state normal frequencies computed at MP2/cc-pVTZ level were scaled by 0.950 while to calculate the oscillator strengths we used state-averaged CASSCF(10,8)/cc-pVTZ electronic wave functions. We used as the average transition energy 6.11 eV, the state-averaged CASSCF electronic transition energy, which compares well with the $S_1 \leftarrow S_0$ transition energy of 4.99 eV [64]. The vertical oscillator strength computed at the equilibrium geometry is 1.14×10^{-3} and the sum due to the contributions from each normal mode amounts to 0.508×10^{-3}, a 45% increase over the vertical value. Vibronic coupling major contributions come from CH bendings (mostly mode ν_4, and mode ν_8), C=O (ν_3) and CO (ν_6) stretchings, with the remaining modes almost not contributing. It is interesting to note that OCO deformation (ν_7) and torsion (ν_9) modes have negative contributions, i.e., they contribute to decrease the band intensity in relation to the equilibrium geometry. This might be due to the geometric distortion upon the transition, with these normal modes being connected to the change from planar to pyramidal shape and the OCO angle decreasing its value. We previously derived negative contributions to the band intensity in a similar calculation of methyl formate [27]. Concerning the most important contributions to the band spectrum, we have just confirmed Ng and Bell [63] suggestions: C=O stretching and CH bendings are the most important contributions to the vibronic spectrum.

Unfortunately, we could not find in the literature any experimental or theoretical value of optical oscillator strengths, either per-mode or total, for this transition. This should be attributed to a very diffuse vibrational structure of the $S_1 \leftarrow S_0$ transition. This diffuseness is due both to the short life time of formic acid in the excited state and to the large geometric change upon the transition [67]. These spectroscopic features,

along with dimerization of HCOOH [63, 67], greatly raise the spectrum complexity. Consequently, the present theoretical calculated oscillator strengths are especially valuable for the formic acid $S_1 \rightarrow S_0$ transition.

It should be noted that the formalism we have presented for the vibronic coupling does not allow the complete calculation of the rate of internal conversion (i.e., its numerical value). However, since the electronic part of the coupling element of the rate of IC is completely equivalent to the acceleration electronic dipole transition moments [49, 68], we make inferences about this process. The acceleration electronic transition moments, together with the velocity and the usual length (Eq. 3) matrix forms, are completely equivalent for exact wavefunctions [69]. Concerning accurate, but not exact, wavefunctions, like the CASSCF functions we used, the three forms should be comparable. Therefore, in the following we use our optical oscillator strengths results, which depend on the square of the electronic transition dipole moments, to obtain relative values of the per-mode contribution to the internal conversion process.

After internal conversion and/or fluorescence, the HCOOH molecule is left with enough energy to overcome the S_0 energy barriers leading to the dissociation channels $CO + H_2O$ (1) and $CO_2 + H_2$ (2). It was recently suggested both experimentally [62, 70] and theoretically [64] that the CH bendings (specially the CH out of plane wagging) and CO stretchings (specially the C=O mode) would be the most important normal modes involved in the vibronic coupling responsible for the internal conversion/fluorescence processes. Although the branching ratio of the reactions (1) and (2) is essentially dynamically independent of the way the molecule at the transition state is initially excited (i.e, random distribution of vibrational states or selective excitation of vibrational modes), as we have shown with our classical trajectory calculations [66], the present results shed light on the details of the internal conversion/fluorescence processes driven by vibronic effects. We see in Table V, specially the normalized optical oscillator strengths per mode column (excluding the equilibrium geometry contribution), that our results fulfill previous expectations:

the CH wagging out of plane (ν_8) and the C=O stretching (ν_3) modes are the most important contributions to the vibronic coupling, that is, to the internal conversion between the S_1 and S_0 electronic states. The other CH bending (CH rock, mode ν_4) and an OH bending (ν_5) have also some contribution, with the remaining modes giving very small contributions or small negative ones.

Summarizing: we have done calculations of the oscillator strengths for the transition between states S_0 and S_1 of formic acid. We have also calculated the contribution to the oscillator strength coming from each mode besides the equilibrium geometry value. Our results show that vibronic effects can increase the oscillator strength value almost 50%, therefore raising the intensity of excitation and radiative decay processes. The main vibronic contribution to the oscillator strength is due to CH bending and C=0 stretching modes, thereby confirming previous spectroscopic assumptions. We have also used these results to rationalize the internal conversion/fluorescence processes between the two electronic states. In particular, we have confirmed the previous suppositions concerning it: The CH bending and the C=O stretching modes are the most important contributions to the internal conversion between states S_1 and S_0.

E. Conclusion

We have discussed an approach to include vibronic effects for calculations of optical oscillator strengths. In this method, the square of the electronic transition dipole moments are directly calculated along the normal coordinates of vibration and then expanded in a polynomial function. After that, analytical vibrational integration using harmonic wave functions, of the square of the transition moments function, allows us to obtain partial (i.e. for each vibrational mode) and total optical oscillator strengths (OOS), for the vibronic transition of interest. We have put forward the possibility of employing this method to discuss internal conversion processes. We have presented applications of the method to valence transitions of benzene (C_6H_6), formaldehyde (H_2CO), acetone (C_3H_6O) and formic acid (HCOOH).

IV. ACKNOWLEDGMENTS

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