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Contributions to the generalized oscillator strength for the inner-shell C $1s \rightarrow 3s\sigma_g$ transition in CO_2 from the vibronic coupling mechanism

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An approach is proposed to account for the general effect of the nuclei motion in the intensity of electronic transitions caused by fast electron collision with molecular targets, following a similar procedure that has recently been used by our group to determine the optical oscillator strength of symmetry-forbidden transition, and which consists of expanding the (squared) transition moment along the normal coordinates of vibration. It is shown that the profile of total generalized oscillator strength as a function of the squared transferred moment can be significantly changed by the inclusion of terms that depend explicitly on the normal coordinates of vibration. The generalized oscillator strength for the inner-shell C $1s \rightarrow 3s\sigma_g$ transition in CO_2 is calculated within this approach and compared with experimental results.

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I. INTRODUCTION

Absolute intensities of photoexcitation processes in atoms and molecules (optical oscillator strength) have been calculated for a long time, first by semiempirical and presently by accurate *ab initio* methods. Most of the calculations for molecules has been performed within the Born-Oppenheimer approximation at the ground-state equilibrium geometry. This approach, despite being very accurate in several cases, does not account, *ipso facto,* for contributions to the optical oscillator strength (OOS) coming from processes with strong contributions from vibronic coupling. These contributions are a manifestation of the fact that molecules are vibrating, and that the dynamics of the nuclei may, for example, cause changes in the selection rules by means of coupling between the electrons and the nuclei movements. These changes in the selection rules are particularly remarkable in certain transitions that, in spite of being forbidden in dipolar approximation, appear in the optical spectra.

Historically, those process with strong vibronic coupling for which the Born-Oppenheimer approximation holds, have been treated by the Herzberg-Teller vibronic coupling theory [1,2] or, more recently, by the direct vibronic coupling approach [3,4], and this kind of situation has been the subject of several experimental optical works [5–11] as well as theoretical calculations [12–20] for different systems. Furthermore, it is important to emphasize that even when the transition is allowed, the vibronic coupling mechanism can contribute significantly to the value of the total oscillator strength [21].

The situation is quite different in what concerns electron impact excitations of molecules, where few experimental work [22–25] has treated this kind of problem and, as far as we know, no theoretical cross-section investigation for processes with strong contributions from vibronic coupling has been appropriately carried out.

The aim of the present work is to extend the procedure, successfully applied to treat vibronic coupling for the optical spectra [4,21,26] to processes involving excitations due to high-energy electron-impact collisions, where the first Born approximation holds. As an application, we present the calculation of the generalized oscillator strength for the inner-shell C $1s \rightarrow 3s\sigma_g$ transition in CO_2, whose cross section is mainly due to the vibronic coupling mechanism, and that has been the subject of recent experimental work [23].

II. THEORY

The present work extends the methodology successfully used before for calculating optical oscillator strength explained in detail in a previous work [4] for electron-impact excitations. The quantity that measures the intensity of a transition resulting from inelastic collisions of molecules with electrons of high energy is the generalized oscillator strength (GOS), which is proportional to the differential cross section. The GOS for the excitation of the ground vibronic state (00) to the νth vibrational state of the nth electronic state is written as

$$f(K,E)_{00\rightarrow n\nu}=\frac{2\Delta E g_n}{4\pi K^2}\int |\langle \chi_{00}(Q)\varepsilon_{0n}(K,Q,\Omega)\chi_{n\nu}(Q)\rangle|^2 \times d\Omega, \tag{1}$$

where ε_{0n} is the scattering amplitude that, in the first Born approximation, is written as [27]

$$\varepsilon_{0n}(K,Q,\Omega)=-\int \psi_n^*(r_1,r_2,\ldots,r_m;Q) \times\left(\sum_{j=1}^{m} e^{ikr_j}\right)\psi_0(r_1,r_2,\ldots,r_m;Q) \times dr_1 dr_2\cdots dr_m, \tag{2}$$

and **K** is the transferred momentum from electron to the molecular target, $\mathbf{K}=\mathbf{K}_{00}-\mathbf{K}_{n\nu}$. $\mathbf{K}_{00}$ and $\mathbf{K}_{n\nu}$ are the incident and scattered momenta, respectively, $\Omega=(\Theta,\Phi)$ represents the orientation of molecules with respect to **K**, $r_1,r_2,\ldots,r_M$ represents the M electron coordinates, Q are the nuclear coordinates, Ψ_k and $\chi_{k\nu}$, respectively, the electronic and vibrational function of the (k,ν) vibronic state.

Summing expression (1) over all discrete and continuum vibrational levels of the n excited electronic state we obtain the total generalized oscillator strength of the entire n electronic band,

$$f(K,E)_{00\rightarrow n}=\sum_{\nu} f(K,E)_{00\rightarrow n\nu}. \tag{3}$$

Usually the experimental electron-impact spectra for inner-shell excitations does not resolve the individual vibronic bands and, in this sense, the experimental results for a specific excited state are presented as differential cross sections or GOS for the entire electronic band, the latter given by Eq. (3).

Using the fact that the vibrational wave functions of the excited state (discrete and continuum) form a complete set, approximating $\Delta\mathrm{E}_{k\nu}$ by $\Delta\mathrm{E}_{k0}$ [4] and neglecting the contribution of the dissociation process, Eq. (3) reduces to

$$f(K,E)_{00\rightarrow n}=\frac{2\Delta E g_n}{4\pi K^2}\times\int\langle\chi_{00}(Q)|\varepsilon_{0n}(K,Q,\Omega)|^2\chi_{00}(Q)\rangle d\Omega. \tag{4}$$

We now express the vibrational function for the ground state as a product of harmonic oscillator eigenfunctions,

$$\chi_{00}(Q)=\prod_{L} \xi_L(Q_L), \tag{5}$$

where $\xi_L(Q_L)$ is the wave function of the L individual normal mode of vibration for the ground electronic sate, and Q_L is the normal mode coordinate.

We also expand the $\varepsilon^2(K,Q,\Omega)$ in terms of the normal mode coordinates of the ground electronic state,

$$\varepsilon_{0n}^2(K,Q,\Omega)=\sum_{L} \varepsilon_{L,0n}^2(K,Q_L,\Omega), \tag{6}$$

and each individual squared scattering amplitude $\varepsilon_L^2\,(K,Q_L,\Omega)$ in a power series of the normal coordinate Q_L,

$$\varepsilon_{L,0n}^2(K,Q_L,\Omega)=\sum_{L}\sum_{j} a_{j,L}Q_L^j. \tag{7}$$

Expressing the ground-state vibration functions $\xi_L(Q_L)$, given by Eq. (5), in the harmonic approximation [4] and integrating over Ω, expression (3) becomes finally

$$f(K,E)_{00\rightarrow n}=\frac{2\Delta E g_n}{4\pi K^2}\varepsilon^2(K,0)+\frac{2\Delta E g_n}{4\pi K^2}\times\sum_{L}\langle\xi_L(Q_L)|\varepsilon_L^2(K,Q_L)|\xi_L(Q_L)\rangle. \tag{8}$$

The integration over Ω is done numerically and results from averaging over the orientation of the molecular axis with respect to vector **K**, i.e., the classical average.

The first term in Eq. (8) is the result that would be obtained when only the equilibrium geometry is used. For optically forbidden excitation processes, this term goes to zero in the limit of the zero transferred momentum, because the generalized oscillator strength tends to optical oscillator strength in this limit,

$$\lim_{K\rightarrow 0} f_{00\rightarrow n}(K,E)=f_{00-n}(E). \tag{9}$$

For larger values of the transferred momentum K, even for an optically forbidden process, the first term in Eq. (8) differs from zero. The second term in Eq. (8) is particularly important for excitation processes with strong vibrational coupling, as is the case of the inner-shell C $1s\rightarrow 3s\sigma_g$ transition in CO_2, whose cross section is mainly due to the vibronic coupling mechanism, treated in the present work. It is worth mentioning that in these cases the GOS profile can be substantially modified when we consider both terms in Eq. (8) instead of only the first one as will be shown in the present work.

A great advantage of the above methodology is that we only need to calculate the electronic matrix elements between the ground and excited states along the normal coordinates of the vibrational ground state. For the optical spectra, we have tested the procedure recently for several inner-shell and valence Herzberg-Teller processes in different molecules [4,21,26]. The calculated oscillator strengths presented an excellent agreement with the experimental results.

III. RESULTS

Single and double configuration-interaction (SDCI) calculations were performed to describe both excited and ground-state electronic wave functions. Molecular orbitals were calculated in a $(12s,6p,1d)/[10s,4p,1d]$ Gaussian basis set [23]. The scattering amplitude was calculated for several geometries along the normal coordinates and fitted to form expression (7). The generalized oscillator strength is obtained by substitution of this function in expression (8).

Figure 1 shows the resulting calculated GOS as a function of the squared transferred momentum compared with the experimental results of Eustatiu *et al.* [23]. A general good agreement is observed with the experimental profile, although the theoretical curve decreases slightly slower than the experimental one. This attests to the reliability of the present method to calculate the GOS for transitions where vibronic coupling effects are important. The result shows, as well, that for inner-shell transitions the first Born approximation has a vast range of applicability, as discussed in details elsewhere [23].

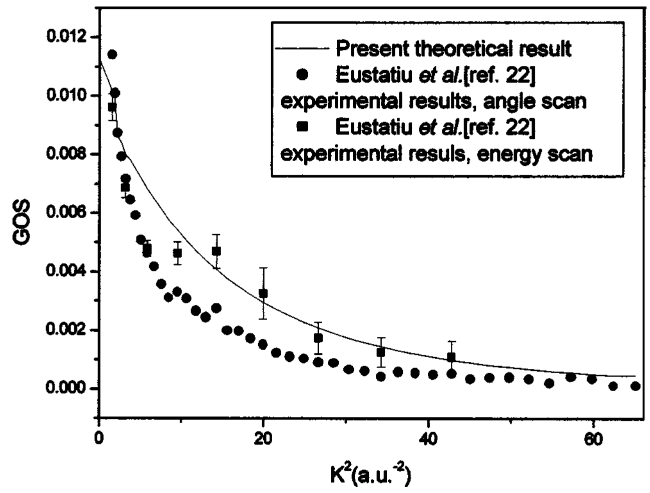

FIG. 1. Generalized oscillator strength for the inner-shell C $1s \rightarrow 3s\sigma_g$ transition in CO_2 as a function of the squared transferred momentum K^2. Full line, present theoretical results; ●, experimental results, angle scan [23]; ■, experimental results, energy angle scan [23].

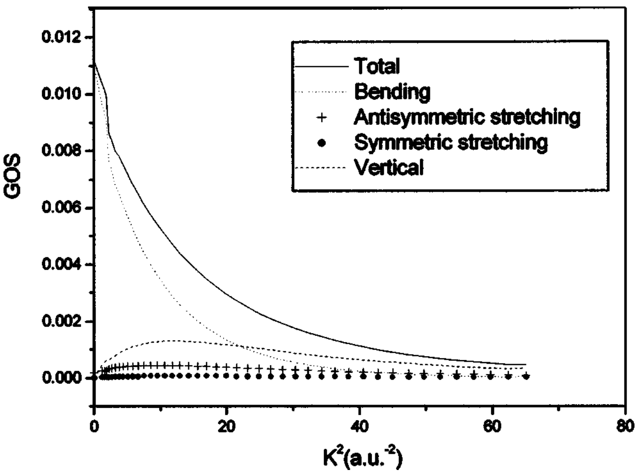

FIG. 2. Contribution per normal modes to the generalized oscillator strength for the inner-shell C $1s \rightarrow 3s\sigma_g$ transition in CO_2 as a function of the squared transferred momentum. Full line, total GOS; ⋯, bending mode; +++, antisymmetric stretching mode; ●●●●, symmetric stretching mode; − − −, GOS calculated at the equilibrium geometry.

Figure 2 shows the contribution per normal modes to the total GOS. It is quite evident that the bending mode gives the principal contribution to the augment of intensity for small values of transferred momentum. This is easily understood since this region is dominated by the dipole term and the most efficient way to increase intensity in this case is by means of vibronic coupling with the high-intensity dipole-allowed C $1s \rightarrow \pi^*$ transition, which is predominately accomplished through the bending mode [4]. The term obtained by using the equilibrium geometry, which is the first term in the right-hand side of expression (8) and which is zero for $K=0$, furnishes the main contribution for GOS at large values of transferred momentum.

As a final comment, we indicate that the present value for the OOS is 0.112, which is slightly different from that one presented in Ref. [4] (0.13). This is due to the fact that in the present work the polynomial expansion of Eq. (7) was carried out to the fourth degree in a denser grid of points, while in Ref. [4] the expansion was truncated at 2° in a less dense grid. The difference is not significant in any way. The experimental value is 0.115 [23].

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