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Angle-resolved electron-energy-loss study of core-level electron excitation in molecules: Determination of the generalized oscillator strength for the carbon $1s(2\sigma_g \rightarrow 2\pi_u)$ excitation in CO_2

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As part of a systematic, quantitative study of the angle dependence of core-level-electron excitation by electron impact, we have determined the generalized oscillator strength (GOS) for the carbon $1s(2\sigma_g \rightarrow 2\pi_u)$ transition in CO_2. The experimental results were obtained at an impact energy of 1290 eV, in the angular range of 2°–14°, with an energy resolution of 0.9 eV. Theoretical values for the GOS were also obtained, using *ab initio* Hartree-Fock molecular wave functions and allowing for the relaxation of all the molecular orbitals in the determination of the excited-state wave function.

I. INTRODUCTION

The excitation and ionization of core-level electrons has played a most significant role in the development of techniques dedicated to the characterization of solid and gaseous samples. Due to the high degree of localization of the orbitals associated with these electrons, the shapes and energies associated with core-level excitation and ionization bands do not show dramatic changes as one moves from the gas to the solid state. This explains why techniques such as electron spectroscopy for chemical analysis and Auger spectroscopy have been intensively applied to the study of both solids and gases [1]. While both these techniques have an ionization process as an initial step, techniques such as extended x-ray absorption fine structure (EXAFS) and near-edge x-ray absorption fine structure (NEXAFS) relay on the observation of photoabsorption features associated with core-electron excitation [2].

Electron-energy-loss spectroscopy has been heavily used for the determination of excitation energies and oscillator strengths of core-level excitations, both at low- and high-resolution conditions [3-5]. This technique has also allowed for the observation of dipole-forbidden inner-shell excitation processes [6]. There has been, nonetheless, only a very limited effort dedicated to the study of the angular behavior of inner-shell electron-energy-loss spectra and to the determination of the generalized oscillator strength (GOS) for inner-shell transitions [7-9].

As part of a systematic study of the angular behavior of core-level electron-impact excitation, we present in this paper the GOS for the C $1s(2\sigma_g \rightarrow 2\pi_u)$ transition in the CO_2 molecule. The GOS has been determined using 1290-eV incident electron energy. Theoretical results have also been obtained, in a first-order Born-approximation (FBA) framework, with the use of Hartree-Fock (HF) molecular wave functions.

II. EXPERIMENT

The same basic experimental procedure previously adopted in the determination of the GOS for valence-shell excitations has been used in the present work [10,11]. Briefly, electron-energy-loss spectra were measured for a given set of scattering-angle values, at a fixed incident energy. The (gas) background contribution was determined by measuring the spectra at the same scattering angles, but allowing the gas to enter the scattering chamber through a side flange, located far from the collision center. This contribution was then subtracted from the raw data. The contribution from the valence-shell excitation processes to the intensity of the inner-shell peaks was determined from a polynomial fitting to the continuum structure observed below the first intense peak, located at 290.7 eV. After these corrections, the area for the $2\sigma_g \rightarrow 2\pi_u$ peak was determined using a Gaussian fitting procedure, previously discussed [11]. As the main interest consisted in the determination of the behavior of the area of this peak as a function of the scattering angle, great care was taken in order to make sure that all the spectra were obtained in the same experimental conditions.

The crossed-beam spectrometer used in the present work has been described before [12]. In order to obtain a higher luminosity and to work in a constant transmission mode, two very important aspects while working with the low intensity, large energy-loss inner-shell excitation processes, a newly developed, Wien-filter-type velocity analyzer [13] was incorporated into the energy-loss spectrometer (Fig. 1) and was accordingly used in the determination of all the inner-shell energy-loss spectra. The Wien-filter analyzer features two three-element zoom lenses. The first one brings the scattered electrons to a fixed pass energy of 30 eV, resulting in an energy resolution of 0.9 eV, as determined by the full width at half maximum for the elastic peak, measured in the same conditions. The second zoom lens reaccelerates the electrons

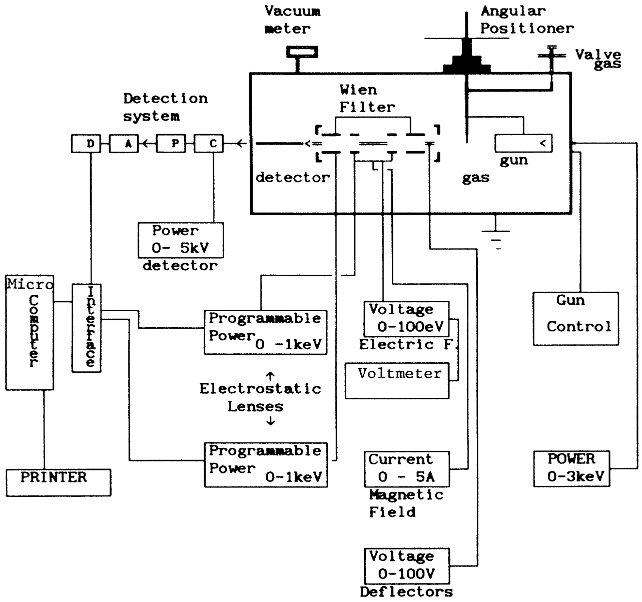

FIG. 1. Block diagram of the electron-impact spectrometer employing the Wien-filter analyzer, where C is the detector circuit, P is the preamplifier, A is the amplifier, and D is the discriminator.

in order to increase the detection efficiency. The energy resolution of the apparatus is limited to 0.5 eV by the thermionically produced incident electrons. In the present case, though, a compromise was attained between resolution and count rate.

The velocity-analyzed scattered electrons are detected by an electron multiplier (Spiraltron, Galileo Electro Optics). The pulses coming out of the detector are fed to a standard electronics (preamplifier, amplifier, discriminator) and are then transferred to the memory of a 16-bit personal microcomputer which is also responsible for the scanning of the voltages in the zoom lenses. The analyzer viewing cone is determined by two parallel circular apertures 500 μm in diameter, located at 120 and 140 mm, respectively, from the scattering center.

In the present measurements, the incident electron energy was 1290 eV and energy-loss spectra have been obtained in the angular range of 2°–14°. The scattering zero-degree angle was checked by measuring the elastic peak area over a 15° range on both the right-hand and left-hand sides with respect to the electron analyzer main geometrical axis. Although a precision mechanism allows the determination of the scattered angle with an accuracy of 0.02°, our angle resolution, defined by the set of apertures in front of the Wien-filter analyzer, is limited to 1.0° in the present experiment.

The scattering volume, defined by the intersection of the electron beam with the effusive gas beam, is small compared to the dimensions of the experimental view cone of the electron analyzer. The interaction geometry is accordingly taken to remain constant as we change the scattering angle.

The experimental uncertainties are estimated in the following manner. The maximum statistical uncertainty was 3.5%, as at least 2300 counts were accumulated at the $2\sigma_g \rightarrow 2\pi_u$ peak, for each scattering angle. Fluctuations in the primary beam current and on the sample pressure were of the order of 1% and 0.5%, respectively. The main source of error is the limited angular resolution (1.0°), which contributes with an uncertainty of approximately 10% to the scattered intensity. The determination of the area of the peak is also subject to a 2% error. The overall uncertainty δ, defined as $\delta=(\sum_i \delta_i)$, is equal to approximately 25% for small angles and 9% for large angles.

III. THEORY

The differential cross section $(d\sigma/d\Omega)_n$ for the excitation of a molecule with N electrons and M nuclei by an electron with kinetic energy E_i is given by the following expression:

$$\left[\frac{d\sigma}{d\Omega}\right]_n=\frac{4}{|\mathbf{K}|^4}\frac{|\mathbf{k}|}{|\mathbf{k}_1|}|\varepsilon_n(K)|^2 . \tag{1}$$

Here n represents the final excited state, $\mathbf{K}$ is the momentum transfer, $\mathbf{K}=\mathbf{k}'-\mathbf{k}_i$, and $\mathbf{k}'$ and $\mathbf{k}_i$ are, respectively, the final and initial momentum vectors for the scattered electron and $\varepsilon_n(K)$ the scattering amplitude.

A very useful quantity is the generalized oscillator strength $f_n(K)$, defined as [14]

$$f_n(K)=\frac{2E}{|\mathbf{K}|^2}|\varepsilon_n(K)|^2 , \tag{2}$$

where E is the excitation energy. The GOS is independent of the incident energy at energies for which the FBA is valid and approaches the familiar optical oscillator strength (OOS) as $K \rightarrow 0$. A very interesting review of the GOS properties can also be found in Ref. 14.

The generalized oscillator strength was calculated from expression (3). As shown in previous cases [15–17], the calculated GOS values depend critically on the quality of the molecular wave functions used in the representation of the ground and excited states.

The molecular wave functions were expanded in a $[(12s,6p,1d)/8s,4p,1d)]$ Gaussian basis set, which includes enough diffuse functions to describe the excited $2\pi_u$ state, and contracted functions to describe the $2\sigma_g$ state. The wave functions were determined at the Hartree-Fock level only, and in this sense, no correlation effects are included in the present calculations. This point is further discussed in Sec. IV. With this basis set, a total energy for the ground state of -187.6869 a.u. was obtained, in good agreement with the value of -187.6803 a.u. determined by England *et al.* [18] and lower than the values of -187.5561 and -187.2985 a.u. determined, respectively, by Winter, Bender, and Goddard [19] and McCurdy and McKey [20].

As the transition we are interested in is associated with the promotion of an inner-shell electron to an unoccupied valence state, it is important to include relaxation effects in the calculations. This means allow all the molecular orbitals to relax in the determination of the excited state associated with the promotion of the C (1s) electron to a valence $2\pi_u$ orbital. It should be emphasized that this state is associated only to a local minimum in the total HF energy for this symmetry, since the real minimum is related to the $4\sigma_g \rightarrow 2\pi_u$ valence excitation process. As a consequence, if we simply apply a standard variational procedure to all the molecular orbitals (MO's), we will obtain a wave function related to the $4\sigma_g \rightarrow 2\pi_u$ process. To bypass this problem we start the calculation with the MO obtained from the ground-state configuration, by promoting a $2\sigma_g$ electron to the $2\pi_u$ level, and freezing all the other MO's. As a next step we freeze the $2\sigma_u$ MO and allow the other MO's to relax. Then we freeze all the MO's except for the $2\sigma_g$ and $2\pi_u$ orbitals, which are allowed to vary, and keep this procedure until no changes in the molecular orbitals are observed, that is, until the local minimum in the HF energy is obtained.

Using this procedure, an energy difference of 292.19 eV was found between the ground- and excited-state HF energies, a value which is close to the experimental result of 290.7 eV [21,22]. When the frozen-core approximation is used, that is, MO's are not allowed to relax, an energy difference of 301.7 eV is obtained.

As a result of the procedure adopted in the determination of the excited-state wave function, the MO's related to this state are not orthogonal to the MO's related ground-state wave function and the FBA matrix element, given by Eq. (2), does not reduce to the FBA matrix element between the $2\sigma_g$ and $2\pi_u$ orbitals. To calculate the matrix element between the ground- and excited-state wave functions, a biorthogonalization procedure was then used [16,17,23].

The optical oscillator strength for this transition was also calculated and found to be equal to 0.167, in good agreement with the experimental value of 0.16 as determined by McLaren *et al.* [24]. The close agreement observed between the experimental and presently calculated values for the excitation energy and OOS indicates that the whole theoretical procedure is indeed consistent.

IV. RESULTS AND DISCUSSION

The CO_2 molecule has a linear geometry in its electronic ground state to which, in a molecular-orbital scheme, the following configuration can be assigned [25]:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4 \; X\,{}^1\Sigma_g^+ \; .$$

The $2\sigma_g$ is a nonbonding orbital, essentially carbon 1s in character. The band associated with the excitation from the $2\sigma_g$ to the unoccupied valence, diffuse $2\pi_u$ orbital, which can be observed at 290.7 eV, entirely dominates the C 1s energy-loss spectrum shown in Fig. 2.

This spectrum has been measured at 1290 eV and at a scattering angle of 4.0°. The main observed structures agree with the previous higher resolution of Wight and Brion [21] and Tronc, King, and Brian [22]. Below the K edge, which is located at 297.5 eV [26], the $2\sigma_g \rightarrow 2\pi_u$ is by far the most intense feature; Rydberg peaks have also been observed by the aforementioned authors, but are not distinguished in the present spectrum. Above the K edge, broad structures can be observed and have been assigned to double excitations and shakeoff processes [21]. The fact that our 4.0° spectrum presents basically the same general shape and relative intensities as observed in smaller-angle measurements [21] shows that indeed inner-shell transitions have a less severe angular dependence as compared to valence-shell excitations.

The GOS for the $2\sigma_g \rightarrow 2\pi_u$ transition has been measured in the K^2 range from 1.4 to 8 a.u. and is shown in Fig. 3, along with our theoretical results. The experimental results have been normalized to the theory at $K^2 = 1.60$, which corresponds to a scattering angle of 3.0°. Table I contains the experimental and theoretical values for the GOS. Within error bars, the normalized experimental values for the GOS present a good agreement with the theoretical results. As mentioned before, a theoretical value for the OOS of 0.167 has been obtained, in good agreement with the experimental result of McLaren *et al.* [24]. It has been assumed that the first Born approximation holds at 1290-eV incident energy. This seems reasonable, if one takes into consideration that the general shape of the spectrum resembles the previous results obtained by Wight and Brion [21], at 2.5-

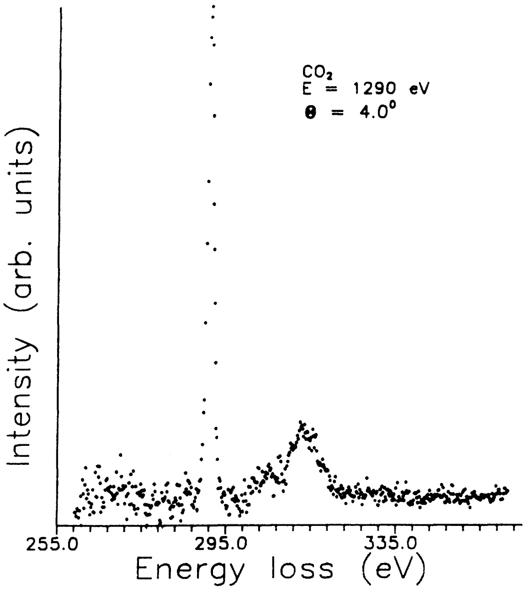

FIG. 2. Energy-loss spectrum of CO_2 at the scattering angle of 4.0° and impact energy of 1290 eV. The intense peak refers to the (C 1s) $2\sigma_g \rightarrow 2\pi_u$ transition.

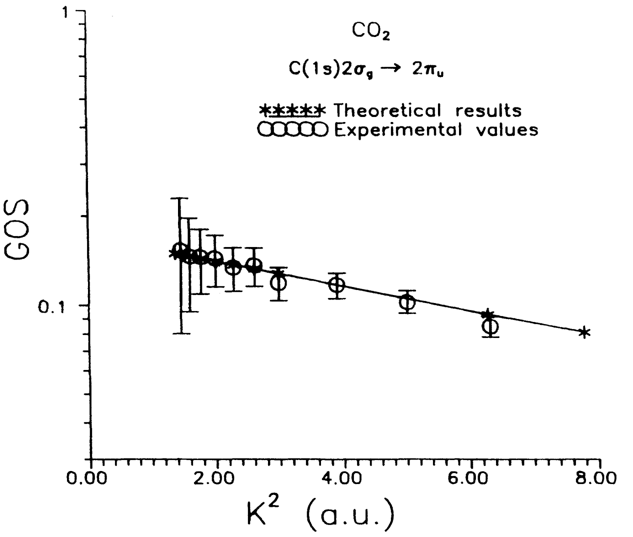

FIG. 3. Generalized oscillator strength (GOS) for the (C 1s) $2\sigma_g \rightarrow 2\pi_u$ transition in the CO_2 molecule.

keV incident energy and close to 0° scattering angle. Besides, it has been also observed, in a study of the GOS behavior for the N 1s excitation in some nitrogen-containing molecules [7,8], that the FBA limit had already been attained at 1400 eV.

Previous C 1s excitation electron-energy-loss studies in the CO_2 molecules have raised the possibility that the final state of the 290.7-eV band would have a bent geometry, and the band would then be associated to a C 1s $2\sigma_g \rightarrow 2\pi_u(6a_1+1b_1)$ transition. This could explain the large full width at half maximum for this band (0.6 eV).

In the present calculation, good results have been obtained for the excitation energy, optical oscillator strength and generalized oscillator strength for this band, assuming a linear geometry both for the ground and excited states. It is well known that in a linear confirmation the $2\pi_u$ state is strongly antibonding [25]; this could eventually lead to a very short lifetime and thence to the observed broadness.

The present results also seem to show that a Hartree-Fock level calculation, with due allowance to relaxation, presents a satisfactory description for both the ground- and excited-state wave functions. This is an interesting observation, as we have shown previously [15-17] that relaxation and correlation effects could play an important role in the calculation of the GOS, specially for inner-valence excitation processes. At least in the present case, the core-level excitation seems to be not very sensitive to correlation effects. This may be related to the fact that the excited electron is associated with the central carbon atom. In the case of the two equivalent oxygen atoms, correlation effects should be important, as seen, for instance, in the N 1s excitation in the N_2 molecule [9].

The subject of calculation of excitation energies and absolute intensities for inner-shell transitions on a self-consistent-field or configuration-interaction basis is of considerable current interest [27]. The present results, obtained with the inclusion of relaxation effects only, may be of interest in this respect. A further study, dedicated to the detailed analysis of the influence of correlation effects in the determination of the GOS for the $2\sigma_g \rightarrow 2\pi_u$ transition in CO_2, is currently under development.

TABLE I. Generalized oscillator strength as a function of K^2 for the C 1s($2\sigma_g \rightarrow 2\pi_u$) transition.

			GOS	
ϑ	K^2	Theoretical	Experimental	Uncertainty
0.03	1.374 24	0.1494		
2.0	1.463 80		0.153	50%
	1.475 01	0.1480		
3.0	1.600 95	0.1462	0.146	35%
4.0	1.768 69		0.145	25%
	1.777 20	0.1437		
5.0	1.997 25		0.144	20%
	2.003 74	0.1405		
6.0	2.276 45		0.134	17%
	2.280 45	0.1368		
7.0	2.606 22		0.136	15%
	2.607 29	0.1325		
8.0	2.986 45		0.119	13%
	2.984 41	0.1277		
10.0	3.897 81		0.117	10%
12.0	5.009 43		0.103	09%
14.0	6.288 06	0.0930		
	6.319 97		0.085	08%
16.0	7.782 51	0.0810		

V. CONCLUSIONS

The generalized oscillator strength for the C 1s ($2\sigma_g \rightarrow 2\pi_u$) transition in the CO_2 molecule has been experimentally determined using 1290-eV electrons and a Wien-filter-type electron velocity analyzer. The GOS was determined as a function of the square of the momentum transfer K^2 in the range of 1.4–8.0 a.u. The excitation energy, optical oscillator strength, and generalized oscillator strength for this transition were also obtained in a first-order Born approximation framework, assuming a linear confirmation for the molecule both at the ground and excited states. A good agreement was found between experiment and theory. In the calculations, the wave functions were allowed to relax, but no explicit introduction of correlation effects has been made.

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