

# Generalized Oscillator Strength for the 18.7 eV

## Electronic Transition in Acetylene

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Determinou-se a Força do Oscilador Generalizada (FOG) para uma nova transição eletrônica na molécula de acetileno observada recentemente em 18.7 eV (A.C.A. Souza & G.G.B. de Souza, *Phys. Rev.* **38**, 4488 (1990)). Como técnica experimental utilizou-se a espectroscopia de perda de energia de elétrons com variação angular, trabalhando-se numa energia incidente igual a 1 keV. A dependência da FOG em relação a  $K^2$  (faixa de 0.05 a 1 a.u.) demonstra o caráter de transição proibida desta banda.

The generalized oscillator strengths (GOS) for a recently reported electronic transition in acetylene (A.C.A. Souza & G.G.B. de Souza, *Phys. Rev.* **38**, 4488 (1990)) has been measured over the momentum transfer range 0.05 to 1 a.u. using angle-resolved electron energy-loss spectroscopy at 1 keV incident energy. The  $K^2$  dependence of the GOS curve demonstrates the dipole-forbidden character of the 18.7 eV band.

**Key Words:** *electron-molecule collisions, Generalized Oscillator Strength, acetylene, quadrupole electronic transition*

### Introduction

The electron energy loss technique is a powerful spectroscopic tool which allows for the study of electronic states occurring at large excitation energies. In particular one is able to study the vacuum ultraviolet and X-ray regions with a single experimental manifold, a difficult matter with the use of conventional photoabsorption techniques. This technique also allows for the determination of excitation energies, cross sections and generalized oscillator strengths for both dipole allowed and forbidden transitions. For large incident energies (as compared to the excitation energies under observation) the First Born Approximation (FBA) will generally hold. Within this approximation the cross section, differential in angle and energy, for the excitation of an atom or molecule to a given electronic state is a function only of the square of the momentum transfer,  $K^2$ , where  $\mathbf{k} = |\mathbf{k}_0 - \mathbf{k}_1|$ ,  $\mathbf{k}_0$  and  $\mathbf{k}_1$  being respectively the initial and final momentum of the scattered electron. A very useful quantity of spectroscopic studies is the Generalized Oscillator Strength (GOS) which is related to the inelastic differential cross section according to the well-known expression<sup>1</sup>:

$$\text{GOS} = (E/2) \cdot (k_0/k_1) \cdot K^2 \cdot (d\sigma/d\omega)$$

where:

$$\begin{aligned} k_0^2 &= 2E_0 \\ k_1^2 &= 2(E_0 - E_1) \\ k^2 &= k_0^2 + k_1^2 - 2k_0k_1 \cos \theta \\ \theta &= \text{scattering angle} \end{aligned}$$

$E_0$  and  $E_1$  are the incident and excitation energies, respectively and  $(d\sigma/d\Omega)$  is the differential inelastic cross section.

It can be shown that the GOS tend to the Optical Oscillator Strength as  $K^2$  tends to zero limit<sup>2</sup>. Experimentally this means the electron energy-loss spectra obtained at high incident energies and small scattering angles will close-

ly resemble the corresponding photoabsorption spectra. As  $K^2$  increases, on the other hand, both symmetry and spin-forbidden transitions become prominent in the spectra<sup>3</sup>. The present experimental conditions (high incident electron energy small scattering angles) is quite adequate for the observation of dipole forbidden, spin allowed transitions. These transitions are basically electric quadrupole - allowed, as evidence by a large body of experimental and theoretical work<sup>2,4-6</sup>. Higher pole excitations can in principle occur but they have been only rarely reported<sup>7,8</sup>. The observation of spin-forbidden electronic transitions, at this impact energy, will usually require very large  $K^2$  values and their contribution to the present data can be safely ruled out.

We have recently taken advantage of the spectroscopic capabilities of the angle-resolved electron energy-loss technique for the study of excited states above the first ionizations potential in atoms and molecules, and the GOS has been determined for vacuum ultraviolet electronic transitions<sup>5,6,9</sup> in  $N_2$ ,  $C_2H_2$ , and Na.

In the case of the acetylene molecule, the GOS and the extrapolated Optical Oscillator Strength were determined for the two very broad structures observed at 13.3 eV and 15.7 eV in the photoabsorption measurements<sup>10,11</sup> and in more recent photoionization studies<sup>12,14</sup>. In order to study these structures, the electron energy-loss spectrum of acetylene was determined in the excitation energy-range of 5 to 50 eV, in the scattering angle range of 1.5 to 7.0 degrees. As a result, a previously unreported band was also observed at 18.7 eV. Based on its angular behavior, the band was associated to a dipole-forbidden, quadrupole-allowed electronic transition. In the present work we confirm the forbidden character of this band through the experimental determination of the GOS. A tentative assignment for the band is also suggested.

### Experimental

The electron energy-loss spectrometer and the experimental technique which have been used in the present

work have been previously described in detail<sup>16,17</sup>. Briefly, it employs a crossed beam technique, in which a beam of 1 keV electrons crosses at right angles a molecular beam of acetylene, formed by the expansion of the gas through a hypodermic needle. The electron beam is produced by a commercial electron gun (Superior Electronics 3K/5U), which has been modified in order to allow for the replacement of the hairpin tungsten filament. The energy resolution, limited by the thermal spread of the thermionically emitted electrons, is equal to 0.5 eV, as determined from the full-width at half maximum (fwhm) of the elastic peak.

The earth's magnetic field is compensated by the use of three mutually orthogonal pairs of Helmholtz coils. These coils reduce the local magnetic field from 250 mGauss to approximately 2 mGauss at the scattering center.

The background pressure is  $1.5 \times 10^{-6}$  torr. When the gas sample is introduced into the vacuum chamber the pressure is raised by one order of magnitude. The gas sample was obtained from White Martins Co. The stated purity was 99.6% and has been used without further purification.

Energy-loss spectra were measured in the angular range of 1.5 to 7.0 degrees. The energy-loss range goes from 5 to 50 eV.

For every angle, each spectrum was recorded as many times as necessary for attaining a good signal-to-noise ratio. The background was subtracted by recording another spectrum at the same experimental conditions but with the gas sample introduced through a side flange far from the scattering center. The zero degree angle was experimentally checked by recording spectra on both positive and negative sides with respect to the electron velocity analyzer axis. The energy-loss scale was calibrated with the use of the well known  $1s \rightarrow 2p$  line of helium.

The scattered electrons are velocity-analyzed by a Möllenstedt electron velocity analyzer<sup>16</sup>. The transmission efficiency of this analyzer is not constant with energy and the intensities, after the background contribution subtraction, were accordingly multiplied by a factor  $f$  (Kollath correction)<sup>18,10</sup>, where:

$$f = (E_0/E_0 - E_i)$$

After application of these corrections, the areas of the elastic peak,  $A_{el}$ , and the inelastic peak  $A_{inel}$ , were obtained through a gaussian fitting procedure. In the determination of  $A_{el}$  it was assumed that the 18.7 eV peak do not interact with the underlying continuum. The contribution from the latter was then subtracted using a previously described procedure<sup>8</sup>.

Absolute values for the inelastic cross sections were determined from the known absolute values for the elastic differential cross section<sup>21</sup>:

$$(d\sigma / d\omega)_{inel} = (d\sigma / d\Omega)_{el} \cdot A_{inel} / A_{el}$$

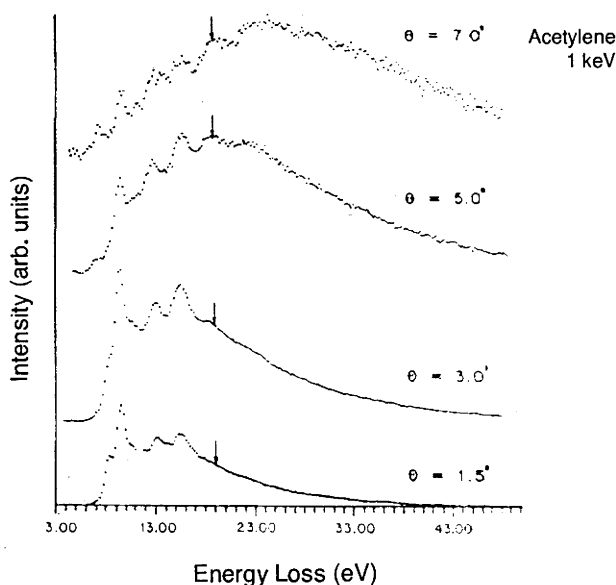
where  $\Omega$  refers to the solid scattering angle.

Errors are estimated to be as follows; statistical uncertainty = 1.5%, primary beam fluctuation = 1.0%, gas pressure fluctuation = 5.0%, scattering angle uncertainty = 20% for  $\theta < 4^\circ$  and 10% for  $\theta > 4^\circ$ . The uncertainties associated to the peak area determination and to the absolute values of the elastic cross section used to normalize the data are respectively, 20%, and 6.0%. The overall uncertainty is thus calculated to be 30% for scattering angles smaller than  $4^\circ$  and 25% otherwise.

## Results and Discussion

The electronic configuration of the ground state of the acetylene molecule is  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 X^1\Sigma_g^+$ . The experimental values<sup>22</sup> for the three lowest vertical ionization potentials are  $(1\pi_u)^{-1} X^2\Pi_u = 11.41$  eV.  $(3\sigma_g)^{-1} A^2\Sigma_g = 16.40$  eV and  $(2\sigma_u)^{-1} B^2\Sigma_u = 18.70$  eV. The dominant contribution associated with the ionization of the  $2\sigma_g$  orbital is located at 23.50 eV and we take this energy to be the ionization potential for the C,  $(2\sigma_g)^{-1}$  state.

The electron energy-loss spectra of acetylene, measured at 1.5, 3.0, 5.0 and 7.0 degrees are shown in the figure 1. Below the first ionization potential the observed peaks are associated with several transitions which have been the focus of extensive previous theoretical and experimental work by several authors and will not be discussed any further in the present paper. The strong and broad structures centered at 13.3 and 15.7 eV are associated to autoionizing, dipole allowed processes. The GOS and the extrapolated optical oscillator strengths for these transitions (assigned respectively to the  $3p\pi_u \leftarrow 3\sigma_g$  and  $1\pi_g \leftarrow 2\sigma_u$  processes) have been recently determined and are presented in ref. 6. An overview of previous photoabsorption and electron impact studies related to the acetylene molecule can also be found in the same reference.



**Figure 1.** Electron energy-loss spectra for the acetylene molecule measured at 1.5, 3.0, 5.0 and 7.0 degrees. The incident energy is 1 keV and the energy resolution 0.5 eV. The arrow points out to the quadrupole-allowed transition at 18.7 eV.

The arrow in figure 1 points out to the new transition centered at 18.7 eV. A comparison with the dipole-allowed transitions at 13.3 and 15.7 eV shows that the relative intensity of the new band increases with increasing scattering angle, being practically zero at the smallest scattering angle. This strongly suggests that this band can be associated to a dipole-forbidden, quadrupole-allowed electronic transition (as mentioned before the contribution of spin-forbidden processes should be negligible in the present experimental conditions). We have determined the GOS for this band, in the 0.05 to 1.0  $K^2$  range, and the

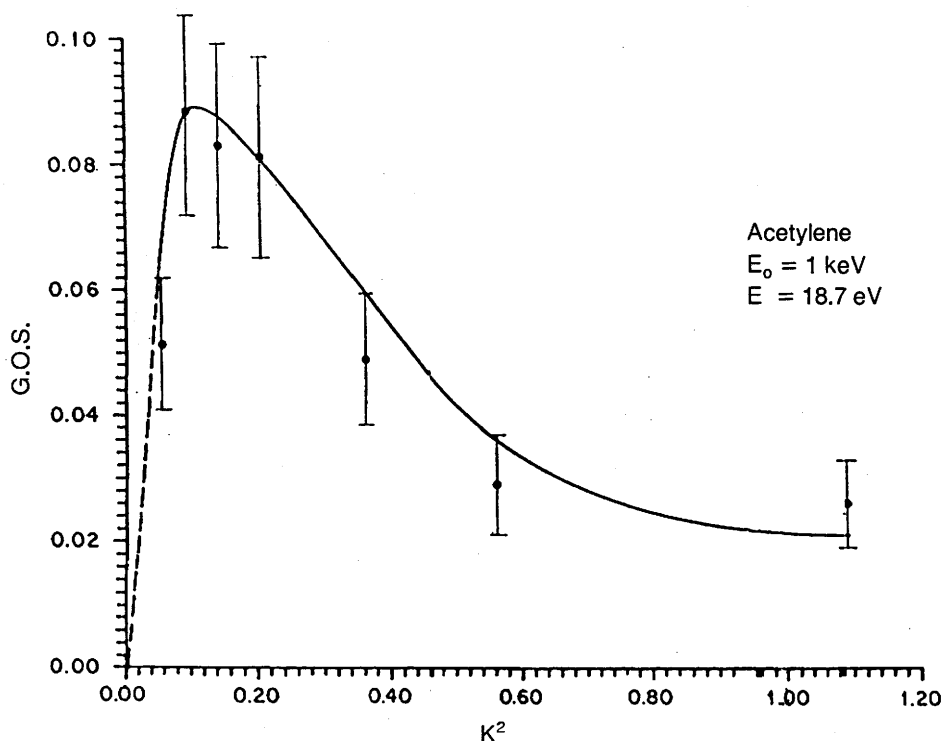


Figure 2. Generalized Oscillator Strength for the 18.7-eV transition.

Table 1:

$\theta^\circ$	$d\sigma_{\text{inel}}/d\omega$	GOS	$K^2$
1.5	2.583	0.051	0.056
2.0	2.682	0.088	0.095
2.5	1.660	0.083	0.145
3.0	1.127	0.081	0.206
4.0	0.395	0.049	0.361
5.0	0.151	0.029	0.561
7.0	0.070	0.026	1.092

results, presented in figure 2, indeed show that this band may be associated with a dipole-forbidden, quadrupole-allowed transition. A definitive confirmation on the quadrupole character of this band would depend of course of the result of theoretical calculations employing molecular wave functions.

An unambiguous assignment for this band is also difficult as it is probably related to a discrete state interacting with one (or more) continua. This is of course true for autoionizing super excited states in general. There have been some calculations on autoionizing (and in some cases shape-resonantly enhanced) states in acetylene but they have been dedicated to dipole-allowed processes<sup>13,23,25</sup>. Our previous work on a similar quadrupole-allowed, inner-valence electronic transition in the nitrogen molecule has also shown the necessity of going beyond the Hartree-Fock level in order to get a quantitative agreement between the experimental and theoretical values for the GOS of such electronic processes<sup>5</sup>. Clearly a theoretical effort is necessary for a quantitative understanding of dipole-forbidden super excited states.

In the absence of theoretical calculations, we tentatively assign the 18.7 eV to  $1\pi_g \leftarrow 2\sigma_g$  excitation. A similar band has been observed in the  $N_2$  isoelectronic molecule at the excitation energy of 31.4 eV and has been as-

sociated to the same process, with contributions from doubly-excited states and (possibly) from the  $\Pi_g$  continuum<sup>5</sup>. In a very approximate reasoning, we also notice that the energy difference between the  $(2\sigma_g)^{-1} C^2\Sigma_g^- = 37.3$  eV<sup>23</sup> and the final state of  $1\Pi_g \leftarrow 2\sigma_g$  transition in  $N_2$  is equal to 5.9 eV. If the same amount is now subtracted from the  $(2\sigma_g)^{-1} C^2\Sigma_g^-$  state in acetylene, we obtain 17.4 eV for the  $1\Pi_g \leftarrow 2\sigma_g$  excitation, a value 1.3 eV smaller than the experimental value. On the other hand, since strong correlation effects are expected to play a significant role on the excitation process of inner-valence electrons, this energy difference may be due to the interaction with double excitations and shake-up processes.

## Conclusions

The generalized oscillator strength (GOS) for a recently reported band in the electronic excitation spectrum of acetylene has been determined, using angle-resolved electron energy-loss technique at 1 keV impact energy. The results show that this band can be associated to a dipole-forbidden, quadrupole-allowed transition. By analogy with an equivalent process observed in the isoelectronic molecule of nitrogen, the new band is tentatively assigned to the  $1\Pi_g \leftarrow 2\sigma_g$  electronic transition.

Dipole-forbidden, super excited states have been observed in several molecules<sup>5,6,27,28</sup>. They are expected to interact strongly with the underlying continua, as has been thoroughly demonstrated in the case of dipole-allowed processes. They should also play a role in autoionizing processes induced by electron impact in gas phase samples. The precise definition of the nature of the electronic states involved in such processes is of paramount importance and remains a challenge to both experiment and theory.

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