

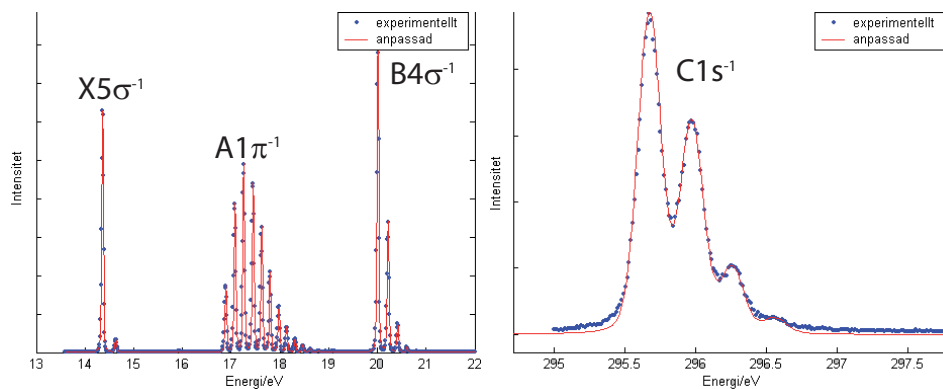
# Project on valence and core electronic structure of diatomic molecules

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## Abstract

In this computer laboration you will combine theoretical models with experimental data to extract relatively much information from two photoelectron spectra. From theories of vibrations in diatomic molecules and spectroscopy, you will define a model with several physical parameters that need to be selected to make the model fit the data as good as possible. This is perhaps a more advanced way of analyzing data than you are used to and it would be impractical to do without computer programs for most of the calculation steps. Therefore, you will learn or refresh some understanding of probability theory and programming too.



## 1 Introduction

*Photoelectron spectroscopy* (PS) is an experimental technique in extensive use. The phenomenon of photoemission was detected by Hertz in 1887. A few years later, in 1905 Einstein was able to explain this phenomenon invoking the quantum nature of light. The light source can be either a gas discharge lamp, an X ray tube or a synchrotron radiation source. The light impinges on the sample, which can be a gas or a surface of a solid, and the electrons emitted by the photoelectric effect are then analyzed with respect to their kinetic energy,  $E_K$ , in an electrostatic analyzer [1, 2].

**Exercise 1.** Explain in a few sentences how a PS experiment is done experimentally.

In this laboration, you will be given two photoelectron spectra of the diatomic molecule, *carbon monoxide* (CO). One is a *valence ionization*, while the other one is a *core ionization* spectra.

Your objective is to, by being creative, extract as much information as possible about CO from these spectra. Some of the information available from this kind of measurements is:

- The binding energy of electronic states in the molecule.
- The lifetime of different electronic states.
- The change in internuclear equilibrium distance (bond length) between the ground and the ionized state.
- Vibrational frequency (harmonic and anharmonic) of electronic states.

## 2 Theory of diatomic molecules

This chapter is supposed to ensure you know enough about molecular dynamics to be able to interpret the spectra. However, this chapter does not give much background. You are expected to know something about the following key concepts from quantum chemistry: *Potential energy surface* (or *-curve*), *Morse potential*, *Harmonic oscillator*, *Franck-Condon region* and *Vibronic transition*.

**Self-test.** Read about the topics that you feel least comfortable with in some book<sup>1</sup> or Wikipedia, at least if you encounter difficulties when reading the following text.

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<sup>1</sup> Perhaps you have some course book for quantum mechanics, molecular spectroscopy or chemistry? One such book is ref. [3].

## 2.1 Vibrational frequency

A diatomic molecule is the simplest possible molecule. The two atoms bound together can be pictured as if they are connected via an elastic spring, which can be stretched and compressed. They must therefore have a *equilibrium distance*,  $r_e$ , where no force is acting on them so their acceleration is zero. If something happens to the molecule, such as an ionization (or excitation), then the force constant,  $k$ , of the spring is changed, and thereby also the  $r_e$ .

In the harmonic approximation, the *potential energy surface* (PES) has the shape of a symmetric parabola

$$V(r) = 0.5 \cdot k(r - r_e)^2 \quad (1)$$

where  $r$  is the internuclear distance. By solving the Schrödinger equation for Eq. (1), we get the eigenenergy values as

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad (2)$$

where  $n$  is the vibrational quantum number and  $\omega$  is the vibrational frequency. From classical mechanics, we have the relation

$$\omega = \sqrt{\frac{k}{\mu}} \quad (3)$$

where  $\mu$  is the reduced mass. However, the harmonic oscillator is only a first approximation to the real molecular potential surface and does not describe the physical properties in detail. A better choice is the Morse potential that correctly describes the strong repulsion of the nuclei at small distances and the dissociation of the molecule which takes place at large internuclear distances.

$$V(r) = D_e \left(1 - e^{-\alpha(r-r_e)}\right)^2 \quad (4)$$

This potential is not symmetric around the internuclear equilibrium distance like the harmonic potential. Here  $D_e$  is the depth and  $\alpha$  is a measure of the curvature of the potential well. It has the eigenenergy values

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_e - \left(n + \frac{1}{2}\right)^2 \hbar\omega_e x_e, \text{ when } n \text{ is not too big} \quad (5)$$

$$\omega_e = \frac{\alpha}{\pi} \sqrt{\frac{D_e}{2\mu}} \quad ; \quad x_e = \frac{\hbar\omega_e}{4D_e} \quad (6)$$

The quadratic term, including  $x_e$ , is a small anharmonic correction and  $\omega_e$  is very close to the harmonic frequency.

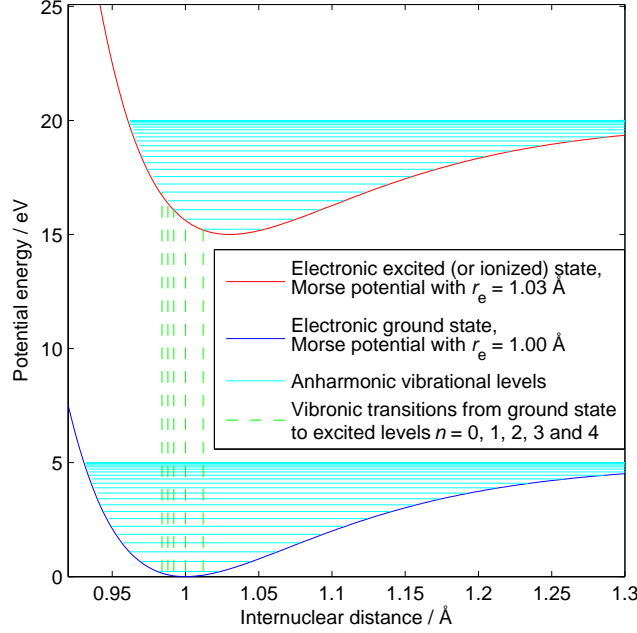


Figure 1: Sketch of potential curves in diatomic molecule. To clearly see the vibrational levels, the following, unrealistic parameter values were used:  $\alpha = 10 \text{ Å}^{-1}$ ,  $\mu = 0.5 \text{ u}$ ,  $D_e = 5 \text{ eV}$ , excitation or binding energy = 15 eV.

## 2.2 Franck-Condon principle

Information about changes in the internuclear distance between ground and ionized states for diatomic molecules, can be found by using the *Franck-Condon principle* (FCP). Classically, it says that the nuclei don't have time to move upon absorption of light, because their mass, and therefore their inertia is much bigger than the electrons'. The FCP implies that in a vibronic transition is more likely to reach excited-state vibrational levels where the nuclear positions are the same in the initial electronic state.

Quantum mechanically, a transition probability is proportional to  $P = \left| \int \Psi_f^* \hat{\mu} \Psi_i dr \right|^2$  where  $\hat{\mu}$  can be the electric dipole operator and  $\Psi$  are the full wavefunctions. Since we are working within the Born-Oppenheimer approximation, we treat electronic and vibrational wavefunctions and selection rules separately and factorize it into  $P = P_{\text{electronic}} \cdot I(n \leftarrow n_{\text{initial}})$ . The electronic transition probability depends on the electronic states and is not discussed further. We turn to the Franck-Condon factor,  $I$ , which within a particular electronic transition gives the relative probability (intensity) to reach each vibrational state  $\psi_{\text{excited},n}$ , when starting from  $\psi_{\text{ground},n_{\text{initial}}}$ : [2, 4, 5]

$$I(n \leftarrow n_{\text{initial}}) \propto \left| \int \psi_{\text{excited},n}^* \cdot \psi_{\text{ground},n_{\text{initial}}} dr \right|^2. \quad (7)$$

A very useful simplification is the *linear coupling model* where both electronic states are described as harmonic oscillators of the same shape, only offset in equilibrium bond length by  $\Delta r_e$ . Non-integral expressions for  $I$  can then be found and for the case of starting in the lowest vibration,  $n_{\text{initial}} = 0$ , the Franck-Condon factor is [6, 7, 4]

$$I_n = I(n \leftarrow 0) = \frac{e^{-S} S^n}{n!}, \quad (8)$$

where  $S$  is called the Huang-Rhys parameter or just Poissonian parameter because equation (8) describes a Poissonian distribution with mean value  $S$ . The value of  $S$  within the linear coupling model is [7, 4]

$$S = \delta^2/2 \quad , \quad \delta = \Delta r_e \cdot \sqrt{\frac{\mu \cdot \omega}{\hbar}} \quad (9)$$

where  $\delta$  is the amount by which the normal coordinates for a particular vibration differs between the initial and ionized states. For a symmetric stretching mode, which is the only kind of vibration in a diatomic molecule, the rightmost equation relates  $\delta$  to the change  $\Delta r_e$  in the real coordinate for bond length, via the reduced mass  $\mu$  and the vibration frequency  $\omega$  (which is the same for both electronic states in the model).

The first peak,  $I_0$ , is called the *adiabatic* peak and is due to transitions to the vibrational ground state ( $n = 0$ ) in the ionized (or excited) molecule. The second peak,  $I_1$ , needs higher photon energy and ends up with vibrational quantum number  $n = 1$ , and so on. The most intense peak is called the *vertical* peak, compare Figure 1.

**Exercise 2.** We assume that in the initial electronic state (ground state), the molecule always has the vibrational quantum number  $n_{\text{initial}} = 0$ . Explain or show with an equation why this assumption is valid.

**Exercise 3.** By using Eq.(8), derive how to get the Huang-Rhys parameter from a spectrum.

**Exercise 4.** Explain how one can retrieve  $\Delta r_e$  from a photoelectron spectrum of a diatomic molecule, where the resolution is good enough to resolve the vibrational states.

Assuming that you know the molecule's vibration frequency in the ground state. How can you then estimate whether  $\Delta r_e$  is positive or negative?

### 3 Combinations of random errors

In the following text, the mathematical tools required for solving the main assignment will be given. It is recommended that you do all calculations in the numerical data-treatment program MATLAB[8], but if you prefer, also other programs can be used such as *GNU Octave*, *IGOR*, *Scilab*, *Origin*, *IDL*, *Mathematica* and many other. Fitting of functions can alternatively be made with *FitXPS*[9].

### 3.1 Convolution

To understand how the various line broadening mechanisms affect the spectra, we first need some probability theory.[10]

Uncontrolled variations in measurements or fundamentally random quantum mechanical effects are described with probability theory. A quantity that in each experimental realization (e.g. each electron detected) has a somewhat random value is called a *stochastic variable*. To be useful we also need a description of its *probability density function* which tells us how likely the different outcomes are.

To take a simple example, let  $A$  be the number of dots that faces up when you have thrown a die. Assuming you don't put the die down in a deterministic way,  $A$  will be a stochastic variable that can take on the integer values 1 to 6. Further assuming the die is ideally manufactured, the probability of getting  $A = x$  is  $P_A(x) = \frac{1}{6}$  for  $x \in \{1, 2, 3, 4, 5, 6\}$  and 0 for all other  $x$ . If we instead add the number of dots from two different dies to get  $C = A + B$ , some work is necessary to derive the probability density  $P_C(x)$ , now for integers  $2 \leq x \leq 12$ .

**Exercise 5.** What is the probability of getting  $C = 8$ , i.e. the value of  $P_C(8)$ ?

**Hint/solution:** If you illustrate all  $(A, B)$ -combinations as  $6 \times 6$ -matrix, with the probability of each combination written in that cell, you can sum up the probabilities of outcomes that give the desired value for  $C$ . For instance  $P_C(3) = \frac{2}{36}$ .

After the above exercise you should recognize the general expression

$$P_C(x) = \sum_{a=-\infty}^{\infty} P_A(a)P_B(x-a) = [P_A \oplus P_B](x) \quad (10)$$

which is the definition of the *convolution* operator  $\oplus$ . Here, the summation can of course be limited to  $1 \leq a \leq 6$  because numbers outside that range have zero probability.

The convolution of two probability densities gives us the probability density for the *sum* of those two independent stochastic variables, so the symbol  $\oplus$  is used for its similarity to the operator  $+$  for the sum of two known numbers. Furthermore, the convolution follows the same algebraic rules as addition (*commutativity* and *associativity*).

For real-valued (not just integer) stochastic variables, the convolution works the same way but the sum becomes an integral:

$$P_C(x) = \int_{-\infty}^{\infty} P_A(a)P_B(x-a)da = [P_A \oplus P_B](x), \quad (11)$$

where  $P_B$  and  $P_C$  now are continuous probability density functions. That means the probability of getting  $A$  in the interval  $a \leq A < a + \Delta a$  is  $\int_a^{a+\Delta a} P_A(x)dx \approx P_A(a)\Delta a$  where the approximation holds for small  $\Delta a$ .

### 3.2 Implementation example

To see how the convolution operator can be implemented in Matlab (and Octave), an example program `combined_broadening_MonteCarlo.m` is provided. This program calculates the probability distribution of a person's position when a train stops, treating the position within the train as uniformly distributed and the train's stop position as normally distributed. Since these two stochastic variables need to be added to get the position with respect to the station, the convolution operator can be used ("Solution 2" in the program). The program also contains a completely different way to simulate the distribution ("Solution 1").

**Exercise 6.** Study the `combined_broadening_MonteCarlo.m` program and run it. Play with other values at least for the `N` and `dx` parameters that describe the number of simulations and the width of histogram bins. Mention some advantage of each solution compared to the other.

(Optional exercise: Can you imagine some kind of statistical problem where a simulation-solution like the first is used rather than operations on probability densities?)

### 3.3 Line broadening

From the name "spectral **line**" it seems there would be no width of the peaks in an ideal measurement. But from Heisenberg's uncertainty principle that measurement would have to last an infinite amount of time, without the state you are looking at decaying into something else or you turning off the light. As a consequence of finite lifetime for excited states, the natural linewidth appears as a minimum width. Then there are of course complications on the molecular level as well as in the apparatus. As you should have learned from chapter 3.1, the convolution operator allows us to express not just the resulting width, but also the resulting shape of a peak in the spectrum, if we can describe the probability densities of all the broadening mechanisms.

Inhomogeneous broadenings are those where each molecule (or photoelectron) is affected independently of the other, specifically *Doppler* broadening (see section 3.4), that the light is not fully *monochromatic* and most other imperfections of the *spectrometer*. These have Gaussian probability density functions,  $f_G(\nu)$ , where  $\nu$  represents frequency or energy. (Since energy and frequency are proportional you can decide the unit, just be consistent)

*Natural* and *pressure* broadenings are instead homogeneous, in the sense that they affect all molecules identically. Their probability densities are Lorentzian functions,  $f_L(\nu)$ .

The Gaussian and Lorentzian probability densities are:

$$f_G(\nu) = \frac{2}{\Gamma_G \sqrt{\frac{\pi}{\log 2}}} \cdot e^{-4 \log(2)(\nu - \nu_0)^2 / \Gamma_G^2} \quad (12)$$

$$f_L(\nu) = \frac{1}{2\pi} \cdot \frac{\Gamma_L}{(\nu - \nu_0)^2 + (\Gamma_L/2)^2} \quad (13)$$

where  $\nu_0$  is the center energy (or frequency) and the width is expressed using *Full width at half maximum* (FWHM)  $\Gamma_L$  and  $\Gamma_G$ . The natural logarithm is denoted `log`, as in Matlab.

**Self-test.** Confirm numerically that the density functions in Eq. (12) and (13) really are normalized and have FWHM  $\Gamma_L$  and  $\Gamma_G$ .

Both Gaussian and Lorentzian functions have the property that when convolving two Gaussians the result is also a Gaussian, and when convolving two Lorentzians the result is a Lorentzian. This means that all the inhomogeneous broadening contributions can be combined into one Gaussian, and all the homogeneous into one Lorentzian.

For instance, the total instrumental line broadening is the convolution of monochromator and spectrometer broadening, both Gaussian with FWHM  $\Gamma_m$  and  $\Gamma_s$  respectively.

**Exercise 7.** Demonstrate numerically for a few values that the relation

$$\Gamma_G^2 = \Gamma_m^2 + \Gamma_s^2 \quad (14)$$

holds for Gaussians.<sup>2</sup> If you want to, you can prove it analytically instead, but the numeric exercise may be a good preparation for the later exercises.

**Hint:** You are supposed to compute the convolution numerically and in some way read out the FWHM. Type `doc conv` in the MATLAB window to get more information of how the `conv(A,B)` command works. A simple self-test could be to use it to solve Exercise 5 again.

### 3.4 Doppler broadening

Doppler broadening is the broadening of spectral lines due to the Doppler effect in which the thermal movement of atoms or molecules shifts the apparent frequency of each emitter. The many different velocities,  $v$ , of the emitting gas particles are following the *Maxwell distribution*

$$f_M(v) = \sqrt{\frac{m}{2\pi k_B T}} \cdot e^{-mv^2/(2k_B T)}. \quad (15)$$

In the non-relativistic regime, the Doppler shift in frequency must be proportional to the velocity according to  $\nu = \nu_0(1 + \frac{v}{c})$ , with  $c$  as the speed of light, meaning that the Doppler profile also is a Gaussian. The broadening is dependent only on the energy of the transition,  $\nu_0$ , the mass of the emitting particle,  $m$ , and the temperature,  $T$ , and can therefore be a method for

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<sup>2</sup>Note: this relation for the Normal distribution is one explanation of why you add the *square* of independent uncertainties in the “error propagation” formula to get a total uncertainty (In Swedish: felberäkning/felfortplantning).



measuring the temperature of a known gas. The *standard-deviation*,  $\sigma_D$ , of the Doppler profile is [11]

$$\sigma_D = \frac{\nu_0}{c} \sqrt{\frac{k_B T}{m}}, \quad (16)$$

where  $k_B$  is *Boltzmann's constant*. The FWHM,  $\Gamma$ , of a Gaussian (Normal) distribution is related to  $\sigma$  by  $\Gamma = 2\sqrt{2 \cdot \log 2} \cdot \sigma$ .

### 3.5 Voigt function

The convolution of Gaussian and Lorentzian gives the *Voigt* density  $f_{G,L}(\nu)$ , that has two parameters to describe its shape.

The pressure contribution is rather small and can usually be neglected. Therefore  $\Gamma_L$  is the natural line-width which is useful since it, with the help of Heisenberg's uncertainty relation, can give the lifetime of the state. The Doppler contribution is also often quite small, so that  $\Gamma_G$  is close to the overall instrumental broadening.

**Exercise 8.** Start with creating a Gaussian and a Lorentzian density function distributed around zero. Let  $\Gamma_G$  and  $\Gamma_L$  be 0.050. Now, convolve the normalized Gaussian and Lorentzian peaks into a Voigt peak. This you can do either by using the expression Eq. (11) or by using the Matlab command `conv(A,B)`. Now plot the normalized result from the convolution together with the Lorentzian (natural line profile) and the Gaussian (instrumental line profile). Redo this for different instrumental broadenings (for example  $\Gamma_G = 0.005$  or 0.10). What has happened to the distribution?

## 4 Data analysis

### 4.1 Preparatory task

Now we are ready to fit a real experimental photoelectron spectrum. If you want to, you can practice on the spectrum of Ar 3p which is a bit simpler than the CO-spectrum, because the peaks are well separated and only two.

If you design a program for automatic fitting in a smart way, e.g. accepting a list of approximative (read out manually) peak center energies and a guess for the width-parameters, it may be helpful to test it on this simple spectrum and then re-use it for the carbon monoxide data. Once the program works, fitting more peaks shouldn't require much more work from you. On the other hand, if you want to make a less sophisticated program where you feel that the more peaks you fit the more manual work is involved, then perhaps you should skip this exercise.

**Self-test.** The file **Ar\_3p.txt** contains a photoelectron spectrum of the argon 3p spin-orbit split lines. The first column is binding energy (ionization

energy) in electronvolts and the second is intensity in an arbitrary unit. Find the energies and both the Gaussian and the Lorentzian FWHM of the lines by fitting a Voigt function in each peak, or even better, fit a sum of two different Voigt functions to the full spectrum. You can compare the energies to the expected ones [12] to name them.

**Hint:** To get the fitting as good as possible you want the residual sum of squared errors,  $\sum_i (d_i - f_i)^2$ , to be as small as possible.  $d_i$  is the experimental data and  $f_i$  is the fitted data, at the energy of frequency  $\nu_i$ .

**Hint:** `fitting_example.m` shows three ways of fitting functions to data in Matlab and can be used as a starting point, although you are free to solve the task in other ways.

## 4.2 Carbon monoxide experiment

The experimental work on carbon monoxide is unfortunately already done, since it is difficult to obtain beamtime for this kind of educational work on research equipment. When using a spectrometer at a multi-user facility such as MAX-II, the instrumental line-broadening mechanisms are usually known<sup>3</sup> with some accuracy. In table 1, these broadenings are specified. As stated in section 3.5, you can assume the Doppler and pressure broadenings are negligible. If you want to, you can try to determine also the Doppler contribution and discuss that result.

The files `CO_C1s.txt` and `CO_valence.txt` contain photoelectron spectra from CO core and valence ionization. For the valence, 120 eV photon energy was used while for the core ionization 360 eV was used. The data files contain one column with binding energy (ionization energy) [eV] and one with intensity [arbitrary unit, maybe number of counts].

**Exercise 9.** Now analyze this data! See page 2 for a list of properties that you can get info about. **Hint:** In the ground state, CO has the equilibrium distance 1.1283 Å, and the vibration frequency 2170.2 cm<sup>-1</sup>.

**Exercise 10.** Discuss differences in the measured parameters between the various electronic states, such as lifetime and vibrational frequency. What can be said about valence electrons' orbital wavefunctions based on these results?

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<sup>3</sup>Because someone has calibrated and tested the instrument before us.

Table 1: Full width at half max (FWHM) of instrumental line-broadening contributions for monochromator  $\Gamma_m$ , and spectrometer  $\Gamma_s$ . Exercise 7 gives  $\Gamma_G$ .

Photon energy [eV]	$\Gamma_m$ [eV]	$\Gamma_s$ [eV]	$\Gamma_G$ [eV]
120 eV	0.015	0.025	0.029
360 eV	0.077	0.076	0.108

Write a report with answers to all exercises and some more explanation about how you did to solve the non-trivial ones. You should at least include the interesting parts of program source code. If your descriptions and programs are clearly presented it can be possible for the examiner to help you or give you scores even when you did a small mistake, while this is not possible if strange results are presented without motivation. If you think it is too much to print, you can e-mail the full programs in a zip-file. Either way, the report should be scientifically understandable without looking at program attachments.

It is always nice to compare to previous experiments, so you have an idea about what to expect and can build upon existing knowledge. Figure 2 is a copy from a book [1] with reference data about valence states in CO and a calibrated photoelectron spectrum taken with a He I discharge lamp<sup>4</sup>.

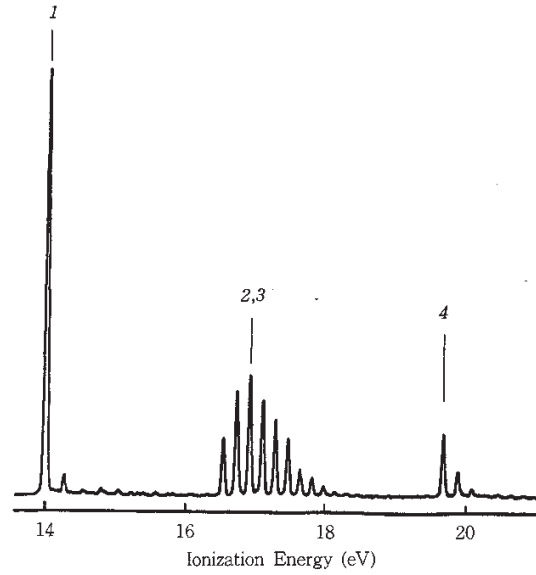
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<sup>4</sup>A “He I”-lamp uses emission from neutral helium excited by discharges from a cathode, particularly the dominating 21.2 eV emission line  $1s2p\ ^1P \rightarrow 1s^2\ ^1S$ . A “He II”-lamp uses the dominating line within  $\text{He}^+$  and analogous names are used for other elements.

## (9) CO Carbon Monoxide



	Exptl. <sup>a)</sup> $I_v$ (eV)	SCF MO [6-31 G] <sup>b)</sup>			CI (Ionic State) [6-31 G] <sup>c)</sup>		
		$-\epsilon$ (eV)	MO	Character	$E$ (eV)	State	Configuration
1	14.01	14.99	5 $\sigma$ (7)	$\sigma_{CO}$	13.11	$1^2\Sigma^+$	0.93(7 <sup>-1</sup> ) -0.15(6 <sup>-1</sup> , 7 <sup>-1</sup> , 9 <sup>1</sup> ) <sub><math>\alpha</math></sub> -0.15(5 <sup>-1</sup> , 7 <sup>-1</sup> , 8 <sup>1</sup> ) <sub><math>\alpha</math></sub>
2	16.91	17.48	1 $\pi$ (6, 5)	$\pi_{bond}$	16.69	$1^2\Pi$	0.95(6 <sup>-1</sup> ) ; 0.95(5 <sup>-1</sup> )
3	16.91	17.48					
4	19.72	21.69	4 $\sigma$ (4)	$n_O$	19.29	$2^2\Sigma^+$	0.92(4 <sup>-1</sup> ) +0.16(6 <sup>-1</sup> , 7 <sup>-1</sup> , 9 <sup>1</sup> ) <sub><math>\alpha</math></sub> +0.16(5 <sup>-1</sup> , 7 <sup>-1</sup> , 8 <sup>1</sup> ) <sub><math>\alpha</math></sub>

a) The spectrum : this work. The  $I_v$ 's : Turner *et al.* (215). See also other works : Turner and May (215 a) ; Carlson and Jonas (54) ; Gardner and Samson (104) ; Edqvist *et al.* (90) ; Potts and Williams (182 a) ; and Natalis *et al.* (165).

b) We used the bond length reported (A 3) ; symmetry  $C_{\infty h}$ .  $E_{SCF} = -112.6672$  hartree. In 4-31 G calculations,  $E_{SCF} = -112.5524$  hartree and  $-\epsilon$ (eV)=14.93, 17.41, 17.41, and 21.60.

c) CI-II. (9, 8)=1 $\pi$ .  $|N\rangle=0.98$ (SCF). The results obtained in other CI levels are given in Appendix B.

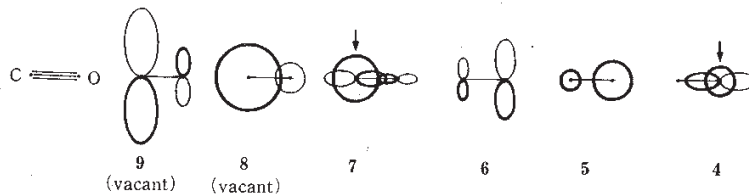


Figure 2: Calibrated photoelectron spectrum of CO valence states taken with a HeI-discharge lamp [1].