

# **SHAPE RESONANCE IN PHOTOELECTRON SPECTROSCOPY**

**Pradipta Sankar Maiti (CY05C012)**

**Sandip Mukherjee (CY05C017)**

**Sanjib Saha (CY05C020)**

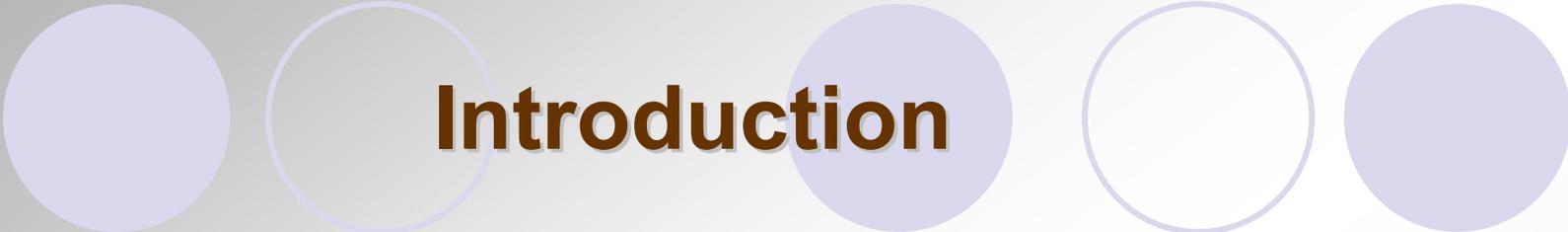
**Shreyasi Dutta (CY05C022)**

**Suman Ghorai (CY05C026)**



# Contents

- **Introduction**
- **What is a Resonance in Quantum Mechanics?**
- **What is a Shape Resonance ?**
- **Evidences of Shape Resonance in PES**
- **Symmetry Resolution Yields Evidence for Shape Resonance**
- **Shape Resonances in Ca & Sb**
- **Evidence of Shape Resonance for the Fourth Band of CO<sub>2</sub>**
- **Conclusion**



# Introduction

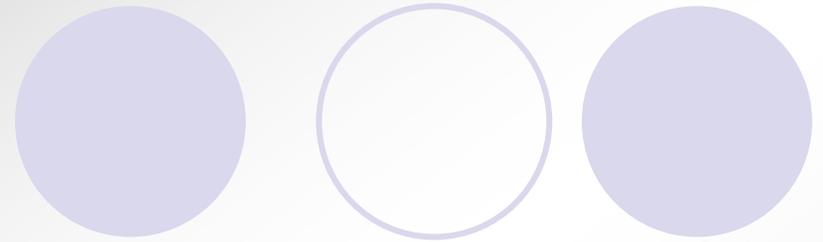
- **Shape resonances are spectroscopic features that have shown promise for probing the geometry of molecules that are not in the gas phase.**
- **For example, shape resonances have been used to determine the orientation of molecules on crystal surfaces.**
- **Another possibility is the use of shape resonances as a convenient "ruler" for measuring non-gas-phase molecular bond lengths.**
- **If a quantitative relationship between bond length and the energy at which a shape resonance occurs could be established, we would have a powerful analytical tool at our disposal.**

# What is a Resonance in Quantum Mechanics?

- A resonance is a quantum state for which the mean energy lies above the fragmentation threshold of a system and is associated with:
  - A) a pronounced variation of the cross-section if the fragmentation energy lies in the neighborhood of the energy of the resonance – the width of this neighborhood is called the width of the resonance.
  - B) a measurable delay of the fragmentation of the system when the system has a mean energy close to the resonance energy – the lifetime (or time delay ) of the resonance is proportional to the inverse of its width.
- Resonances are usually classified into shape and Feshbach resonances or into Breit-Wigner and Fano resonances.
- The classification makes sense only if the lifetimes of the resonances are not larger than the typical vibrational time of the system. Otherwise the situation is much less clear due to overlapping resonances.

# What is a Shape Resonance ?

- The shape resonance arises from an electron excited into an electronic state from which it tunnels through a centrifugal molecular potential barrier into continuum and can be predicted within the framework of a single electron model.
- Experimentally, shape resonances are seen as broad peaks in the cross section curve. The identification of a shape resonance is best carried out through the study of the partial cross sections of the individual molecular orbitals rather than total cross section. In addition, shape resonances strongly affect the angular distribution of the ejected photoelectrons.
- Shape resonances were first predicted for diatomic molecules but similar effects are also found in case of polyatomic molecules.
- Shape resonances are expected both in the photoionization of valence and core shell orbitals.



If the ground state of an electronic system can be labeled by  $\alpha^2p^0$  with  $\alpha$  a doubly occupied orbital and if  $f_E$  corresponds to an incident electron of kinetic energy  $E$ , then:



( Shape Resonance )



(Feshbach Resonance)



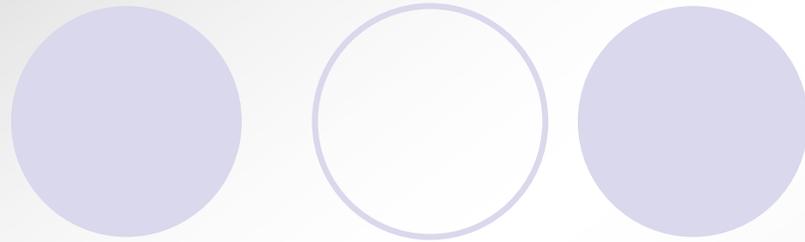
(Core Excited Shape Resonance)

# Evidences of Shape Resonance in PES

- **Shape resonances in the core excitation of small molecules have been of considerable interest, especially in light of the suggestion that the position of the resonance above threshold is related to the size of the molecule and, thus, could be used as a ruler to measure molecular dimensions.**
- **Subsequent discussion has raised questions about the criteria for establishing that a particular structure in a photoabsorption spectrum is a shape resonance or not and has been thus a subject of much controversies.**

# Symmetry Resolution Yields Evidence for Shape Resonance

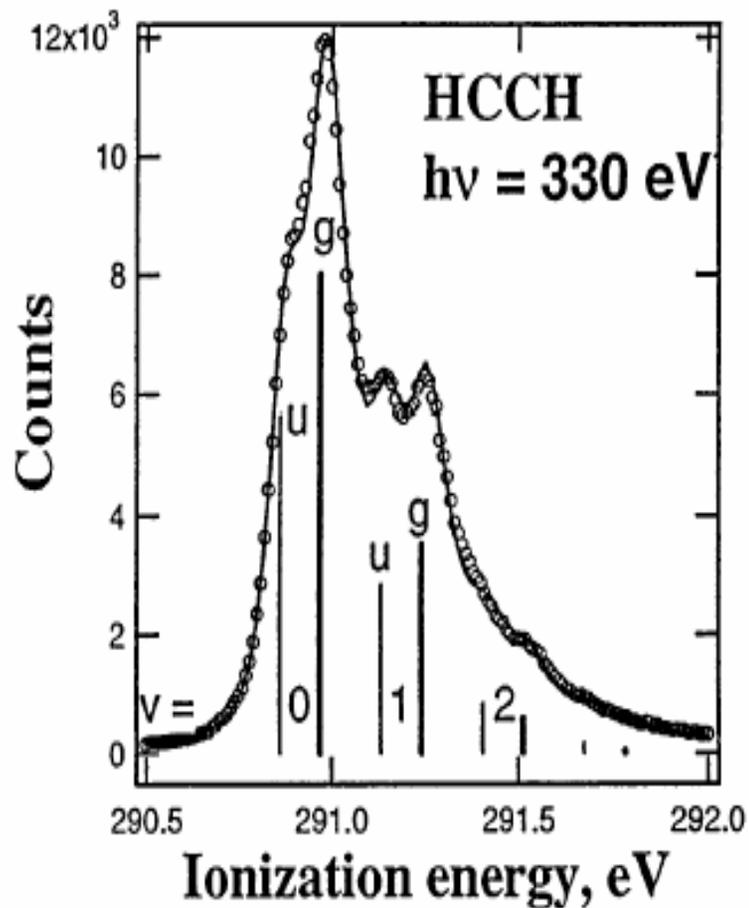
- High-resolution measurements of the C 1s photoelectron spectrum of ethyne (acetylene) at photon energies between 297 and 348 eV have been analyzed to give the energy dependence of the relative cross sections for ionization of the  $1\sigma_g$  and  $1\sigma_u$  orbitals.
- The  $1\sigma_u^{-1}/1\sigma_g^{-1}$  intensity ratio is greater than 1 at the lowest photon energies but reaches a minimum of about 0.6 between 315 and 320 eV.
- These results can be understood in terms of the effect of shape resonance on the ionization cross-section and provide quantitative information on the position and magnitude of such resonances.



- Carbon 1s photoelectron spectrum of HCCH at a photon energy of 330 eV.

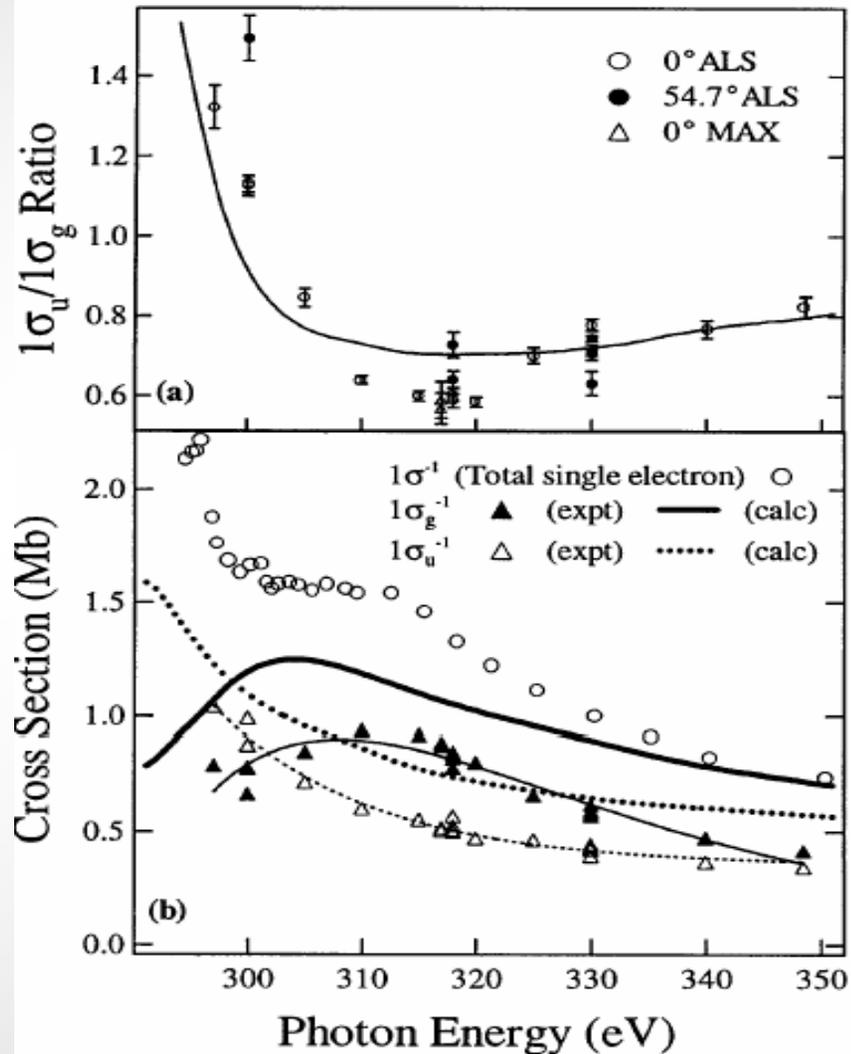
- The points represent the data and the solid curve a fit assuming that carbon-carbon stretching is the only mode contributing to the vibrational structure. The data and the fit extend to both higher and lower energies than shown here. The vertical bars indicate the position and intensity of the different vibrational transitions.

- The light lines are for  $1\sigma_u^{-1}$ , and the heavy lines are for  $1\sigma_g^{-1}$ . The intensities shown for  $\nu=2$  and  $\nu^g=3$  contain contributions from CH stretching modes, which were not considered in the fitting procedure.



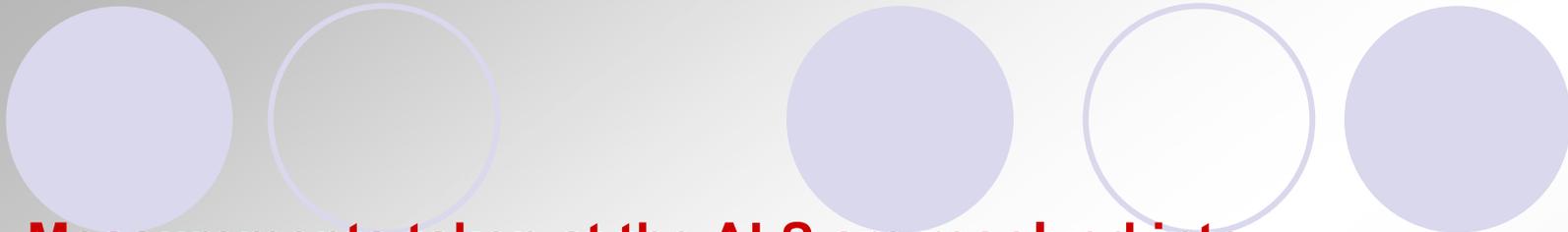
(a) The ratio of the cross sections for ionization of the  $1\sigma_u$  and  $1\sigma_g$  electrons of ethyne as a function of photon energy. The open circles represent  $0^\circ$  results for HCCH. The closed circles show  $54.7^\circ$  results for both HCCH and DCCD. The triangles are derived from  $0^\circ$  data for HCCH and DCCD from Ref. [2]. The solid line shows a theoretical calculation from results given in Ref. [1].

(b) Cross section for carbon  $1s$  ionization in HCCH. Open circles represent the total single hole cross section, from Ref. [3]. Triangles show the cross section for ionization of  $1s_u$  (open) and  $1s_g$  (closed). The heavy solid lines show theoretical results from Ref. [1], and the light lines are smooth curves drawn to show the overall trends



[1] R. E. Farren, Ph.D. thesis, Indiana University, Bloomington, 1989.

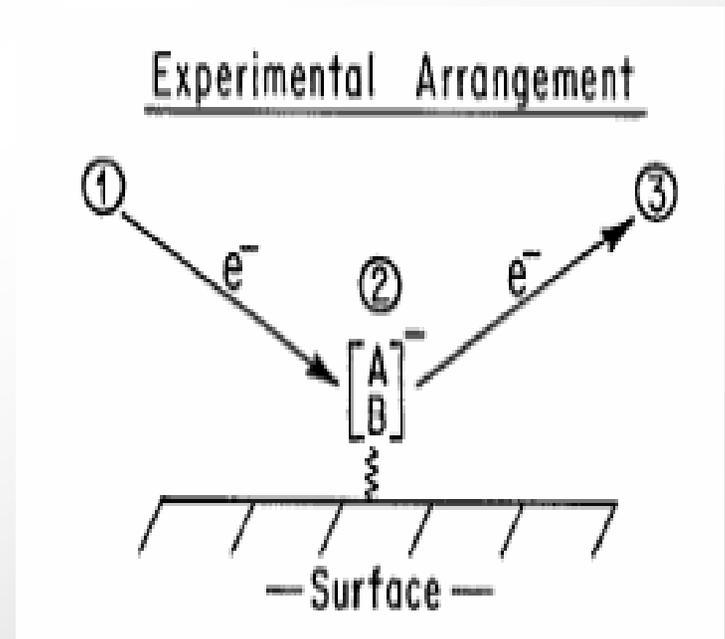
[2] T. D. Thomas, L. J. Sæthre, S. L. Sorensen, and S. Svensson, J. Chem. Phys. **109**, 1041 (1998).



- **Measurements taken at the ALS are resolved into contributions from electrons of g (symmetric) and u (antisymmetric) character, as shown above. According to dipole selection rules, transitions to the shape resonance can result only from ionization involving electrons of g character ("1 $\sigma_g$ " ionization). Thus, the observation of enhanced 1 $\sigma_g$  ionization (i.e., larger 1 $\sigma_g$  cross section) at the predicted energy would provide strong support for the existence of a shape resonance. A plot of 1 $\sigma_u$  / 1 $\sigma_g$  vs. photon energy shows a minimum (i.e., 1 $\sigma_g$  is at a maximum) at about 317 eV, which coincides with the location of the shape resonance indicated by previous investigations and is slightly higher than predicted by theory.**
- **This result clearly demonstrates how the improvements in spectral resolution made possible by the ALS can help resolve outstanding questions in the scientific literature and lead to better understanding of the inner workings of molecules.**

# Shape resonance enhancement of vibrational excitations for CO chemisorbed on Ni(III) probed via inelastic electron scattering

- This experiment examines how the formation of a transient negative ion during the scattering of an electron from CO chemisorbed on Ni(111) can lead to significant enhancement in the probability for vibrationally inelastic scattering.



- 
- **Under resonant scattering conditions, the incident electron is attached to a quasibound state of the molecule/surface system.**
  - **Shape resonances, which involve injection of the incident electron into a previously unoccupied orbital of the adsorbate without further modification of the core electron distribution, are particularly attractive for such studies. Here, e.g., if the electron is placed in an antibonding orbital of the adsorbate, the internuclear separation of the negative ion state will be extended relative to that of the ground state.**
  - **When the electron escapes, the molecule is abruptly returned to the ground state with modified nuclear coordinates and consequently may be vibrationally or rotationally excited.**
  - **Such shape resonances have been observed for various physisorbed and chemisorbed molecules on surfaces.**

# Shape resonance in Ca and electron affinity in Ca ( $1S$ )

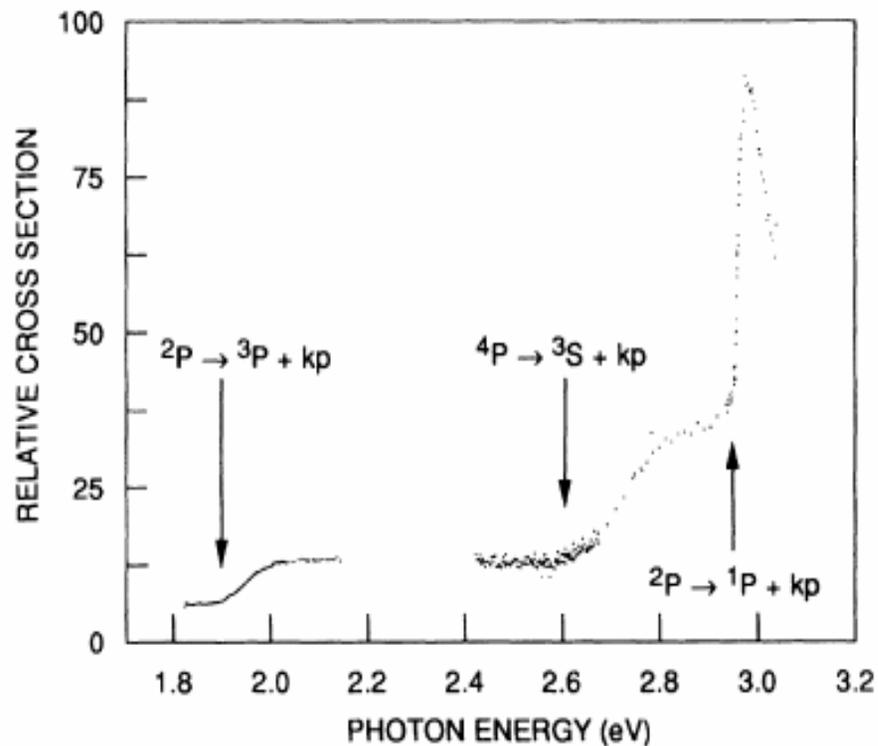


FIG. 1. Total photodetachment cross sections above 1.8 eV; arrows indicate various thresholds from  $^2P$  and  $^4P$   $Ca^-$  beam components. Note the shape resonance near 2.9 eV.

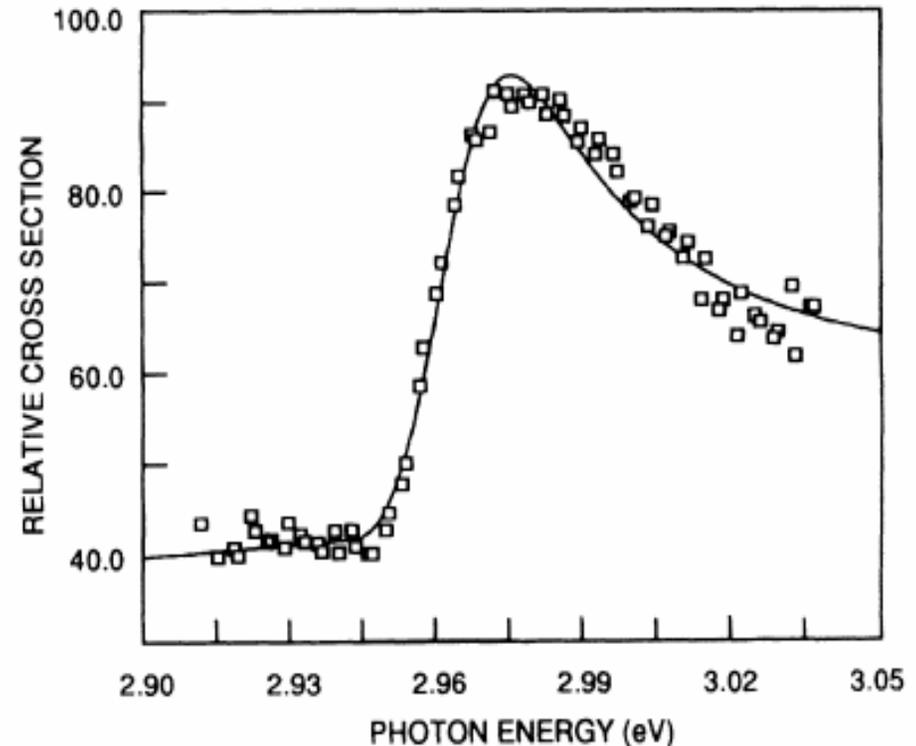


FIG. 2. Data in the region of the shape resonance, and a fit to them using the modified threshold law, Eq. (2), to obtain  $E_R$  and  $\Gamma/2$ .

# Shape resonance in Sb (0001)

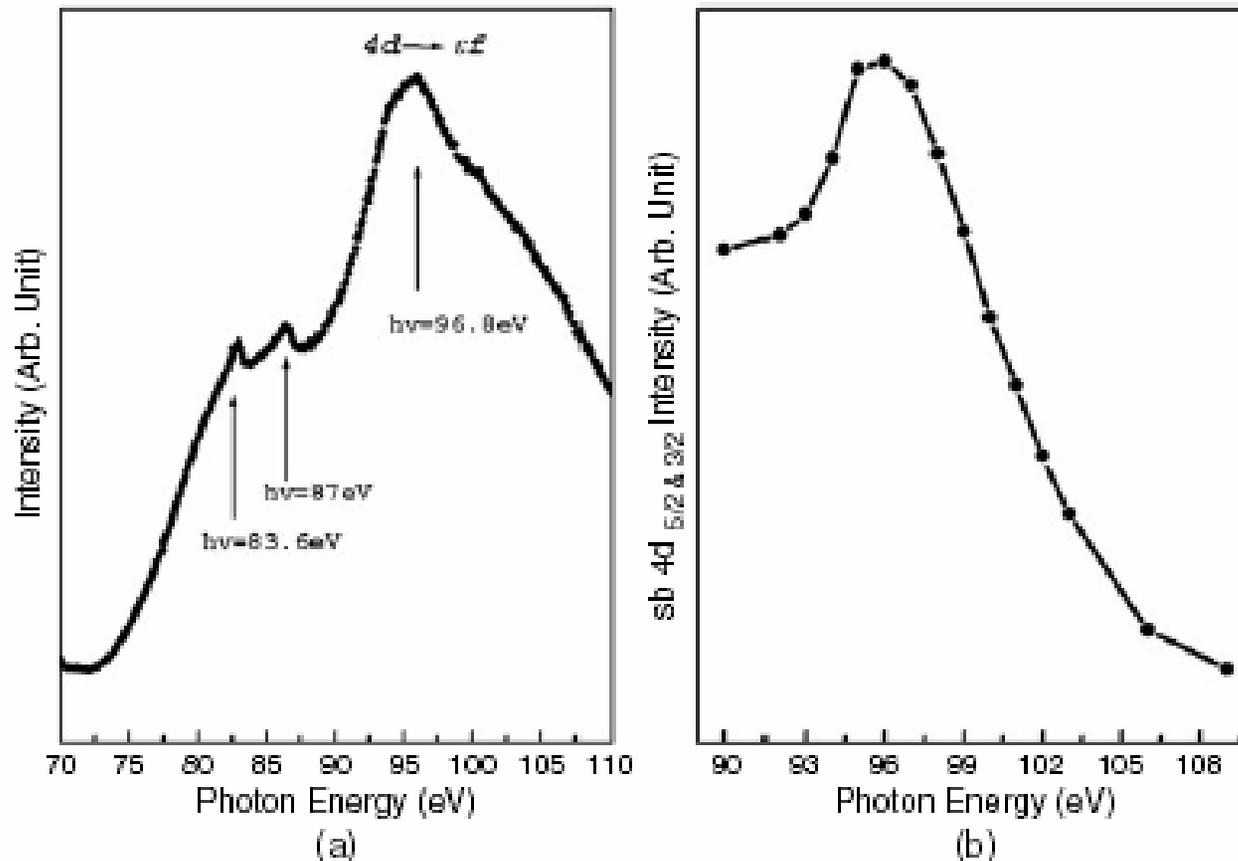
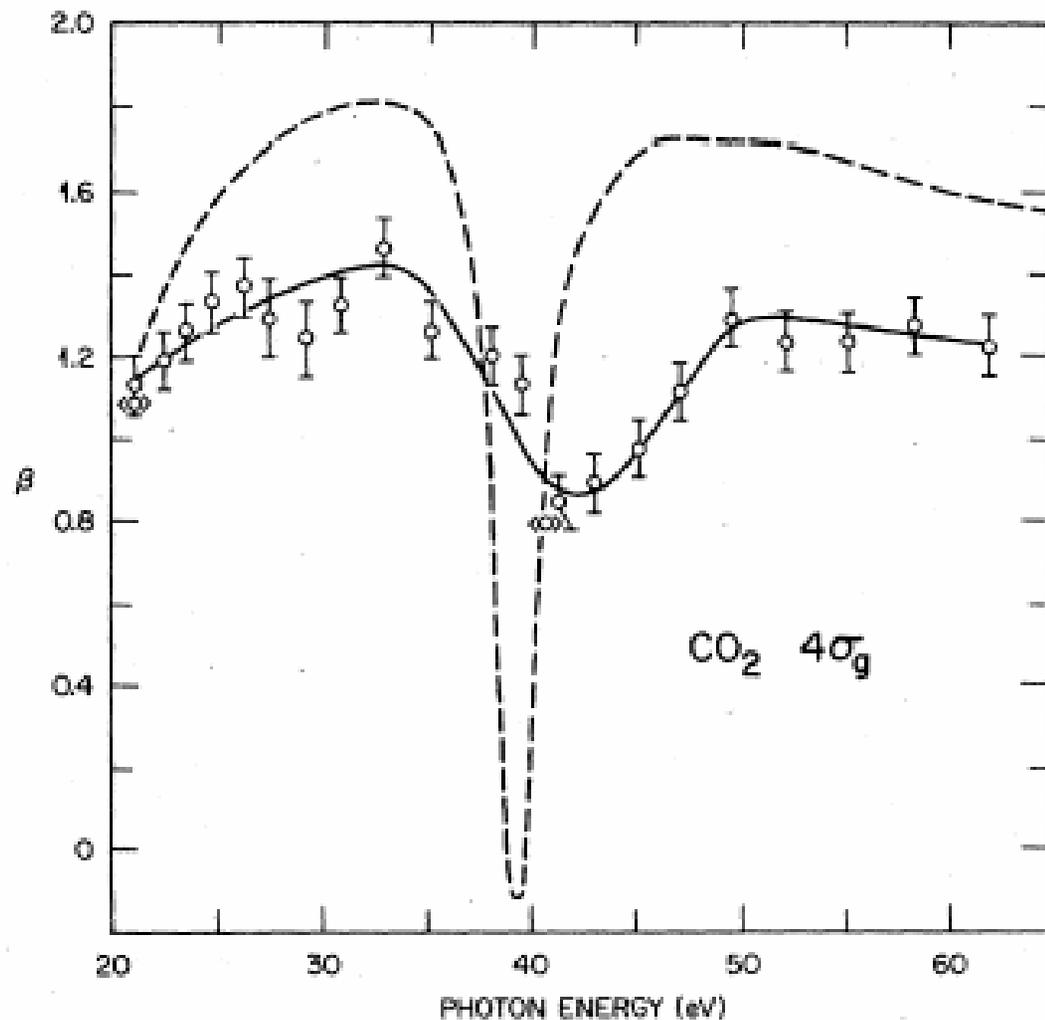


Figure 1. (a) X-ray absorption of Sb(0001) in total fluorescence yield mode obtained in the photon energy range of the Sb  $4d \rightarrow \epsilon f$  shape resonance. (b) The integrated intensity, obtained by integrating peaks of Sb  $4d_{5/2}$  and Sb  $4d_{3/2}$  of the Sb 4d photoemission (PE) peaks, is shown as a function of photon energy.

# Evidence of Shape Resonance for the Fourth Band of CO<sub>2</sub>

- Predictions of the shape resonances were first done for the diatomic molecules and then extended to the polyatomic ones.
- Experimentally features in the partial photoelectron cross-section curves for the outermost orbital in both CO & N<sub>2</sub> were identified as shape resonances, but evaluation of the comparison was hampered by additional structure in the experimental curve.
- Thus the very strong shape resonance predicted for the fourth band in the photoelectron spectrum of CO<sub>2</sub> was welcomed as an ideal test between theory and experiment.
- Calculations also showed an enormous dip in the angular asymmetry parameter  $\beta$  near 40 eV using a synchrotron radiation. Then it was verified with the experiment showing the Shape Resonance effect.

Figure: Angular asymmetry parameter obtained for the fourth band of the photoelectron spectrum of CO<sub>2</sub> representing the C<sup>2</sup>Σ<sub>g</sub><sup>+</sup> state of CO<sub>2</sub><sup>+</sup> is plotted as a function of photon energy. Experimental data are given by the open circles with the error bars that reflects the uncertainty in reproducibility. The dashed lines represents the calculated values on the basis of the multiple-scattering method.



$$\beta = \frac{4(R - 1)}{3P(R + 1) - (R - 1)}$$

$R$  is  $I(0^\circ)/I(90^\circ)$

# Significance of shape resonance

Many people are familiar with acetylene as a welding fuel, but it also plays an important role in industrial chemistry. Acetylene molecules that are fixed (adsorbed) onto a specially prepared surface serve as the foundation for the synthesis of certain types of plastics, such as polypropylene. To achieve the desired end result, the initial conditions of the acetylene molecules on the surface must be well understood. It would therefore be extremely useful to have a simple way to determine the properties of these molecular building blocks.



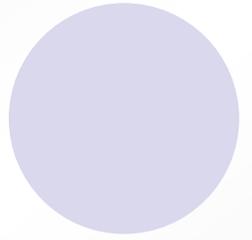
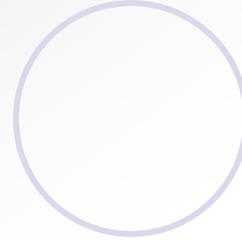
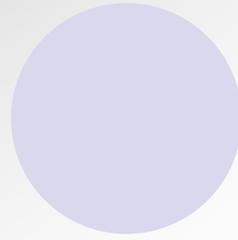
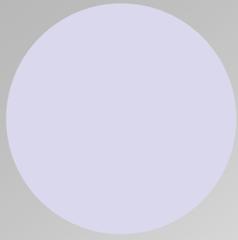
# Conclusion

- **The identification of elusive spectroscopic features known as shape resonances, once touted as a tool for measuring molecular bond lengths, has over the years proven to be controversial.**
- **But in the recent past some convincing evidences for the existence of shape resonances specially in small molecules have been obtained through high resolution photoelectron spectroscopy, where small splittings in molecular energy levels can be resolved.**



# References

- T. D. Thomas, N. Berrah, J. Bozek, T. X. Carroll, J. Hahne, T. Karlsen, E. Kukk, and L. J. Sæthre. *Phys. Rev. Lett.* 82, **1999**
- Bongjin S Mun, Guorong V Zhuang, Philip N Ross, Zahid Hussain, Renaud Guillemin and Dennis Lindle. *Phys. Rev.* 16, **2004**
- Jeong Sook Ha and S. J. Sibener. *J. Chem. Phys.*, 98, **1993**
- Edward I. Solomon, Lipika Basumallick, Peng Chen, Pierre Kennepohl. *Coordination Chemistry Reviews* 249, **2005**



Thank You