Shape Resonances of Oriented Molecules: *ab initio* Theory and Experiment on Hydrocarbon Molecules

N. Haack, G. Ceballos, H. Wende,* and K. Baberschke
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany

D. Arvanitis
Department of Physics, Uppsala University, S-75121 Uppsala, Sweden

A. L. Ankudinov and J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98185-1560

(Received 22 July 1999)

We report *ab initio* calculations of the x-ray absorption cross section for the near edge x-ray absorption fine structure of C_2H_6, and C_2H_4, and C_2H_2 at the C K-edge, based on a full multiple scattering formalism. The angular dependence of the electric dipole transition in the calculations as well as the angular dependent experiments for the oriented molecules give a good opportunity to compare both. The resonance can be assigned to a σ^* shape resonance. The multiple scattering formalism and the experiment agree well and thereby support the existence of such features in the spectra.

PACS numbers: 33.80.–b, 71.15.–m, 78.70.Dm

The broad structures in the continuum region of the x-ray absorption spectra of molecules have been the focus of many studies in the past. Since the contributions of Dehmer *et al.* [1], a widely accepted interpretation is that these resonances originate from the temporary trapping of the excited core electron by a centrifugal barrier of the molecular potential in a quasibound state. An important part in the discussion concerning this so-called σ^* shape resonance is played by the linear hydrocarbon molecules ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2), as they are considered as a paradigm for systems with a single, double, and triple bond, resulting in a systematic variation of the C-C bond length $d_{\text{C-C}}$. In this way, one is able to investigate directly the influence of the molecular geometry on the experimental results. Numerous experimental [2–9] and theoretical [10,11] studies have been performed on C_2H_6, C_2H_4, and C_2H_2. In order to analyze the NEXAFS spectra, a quantum mechanical scattering model was suggested [5,9], based on the principle of the "giant resonance" by Connerade [12]. This simple model worked satisfactorily, as it reproduced the asymmetric line shape with high energy tail, a result of general considerations in the theory of scattering from a bound state into the continuum (a quasibound final state). Here we advertise that the angular dependence of such an electric dipole transition can be measured easily for oriented molecules. In the same way, the calculation allows us to align the x-ray **E** vector parallel or perpendicular to the molecular bond axis. This combination of theory and experiment became available only recently with advances in computational codes and is presented here for the first time for the prototype of the linear hydrocarbons.

Recently, the existence of this resonance in the photoabsorption spectra of C_2H_6, C_2H_4, and C_2H_2 has been questioned by Kempgens *et al.* [13,14], who measured the photoionization cross section of the C $1s$ main line (single hole). The authors concluded that the broad feature in the absorption spectra of these hydrocarbons is caused by multiple electron excitations. This interpretation is contradictory to the results presented by Sorensen *et al.* [15]. Separating the C $1s$ photoelectron spectrum of C_2H_4 into contributions from the C-C and the C-H stretch modes, the authors found a non-Franck-Condon-like behavior in the resonance region and took this as an indication for the presence of a shape resonance. In another study, Thomas *et al.* supported the existence of such resonances by measurements of the photon energy dependent $1\sigma_u/1\sigma_g$ intensity ratio in the C $1s$ photoelectron spectra of C_2H_2 [16].

Our present calculations were performed with the program FEFF8 [17]. Using this code, the x-ray absorption coefficient $\mu(E)$ in the near edge region (NEXAFS) as well as the extended energy range (EXAFS) can be calculated. The theory is based on a relativistic Green's function formalism, using an *ab initio* self-consistent field (SCF) real space multiple scattering approach for a defined cluster of about 100 atoms. The free atom potentials of each atomic type are calculated self-consistently, using a relativistic Dirac-Fock atomic code. The total muffin-tin scattering potentials are obtained iteratively, by successive calculations of the density matrix and then the potential until self-consistency is reached. These SCF potentials are essential for an accurate determination of the Fermi level. For the purpose of improved calculations of NEXAFS spectra, a full multiple scattering (FMS) approach is implemented into the code. FEFF8 calculates the excitation of a photoelectron in a muffin-tin-like scattering potential of the cluster for a fully relaxed core hole. It does not include multiple electron effects such as shakeup excitations. An earlier version of this *ab initio* code, not including FMS, was used to calculate the photoabsorption cross section of other small molecules such as N_2 and O_2 [18,19]. Here we use the advanced version (full matrix inversion, self-consistent potential calculation) and present the first angular dependent and variable cluster size calculations, i.e., study the effect of stretched C-C bond, the H atoms, as well as the Cu substrate.

Figure 1 shows the C 1*s* NEXAFS spectra for a single free molecule of C_2H_6, C_2H_4, and C_2H_2 calculated for different orientations [$\Theta = 0°, 10°, 45°, 90°$; see inset of Fig. 1(b)]. The molecular geometry was taken from [20]. The intensity of the calculated cross section ($T = 0$ K) is given in absolute units of Mbarn. For all three hydrocarbons, a broad feature in the continuum regime is visible, which shows an asymmetry with a tail on the high energy side. A clear angular dependence of this structure can be recognized, having a maximum intensity for the **E** vector parallel to the C-C bond ($\theta = 90°$), decreasing for 45° and 10° and vanishing completely for $\theta = 0°$. This behavior is in correspondence to predictions for the angular dependence of a σ^* shape resonance [2,6,21]. The asymmetric line shape of the peaks can be understood in analogy to the model of "giant resonances" of Connerade *et al.* [12,22]. This model has been found to be qualitatively valid also for molecular continuum resonances such as the σ^* shape resonance [23,24]. As mentioned above, the different bondings between the C atoms in the three hydrocarbons lead to varied bond lengths, namely, 1.533 Å (C_2H_6), 1.337 Å (C_2H_4), and 1.203 Å (C_2H_2) [20]. It can be observed from Fig. 1 that the maximum position E_{max} of the resonance changes with $d_{\text{C-C}}$, moving to lower energies for larger bond length, in agreement with the scattering picture of the potential well (Table I). For C_2H_2, it is located at 311.6 eV, shifting to 301.8 eV for C_2H_4 and to 294.1 eV for C_2H_6. Such a linear correlation between E_{max} and $d_{\text{C-C}}$ was already derived empirically by gas-phase experiments [3] and is now confirmed by the present *ab initio* calculations. The dependence of this continuum resonance on the C-C bond length and its angular dependence led us to the conclusion that it can be assigned to a σ^* shape resonance. Our calculated values of the ionization potential (IP) for the three molecules, given in column 2 of Table I, are in a remarkably good agreement with the well-known IP values (column 1). This means that the self-consistent calculation of the molecular potential determines the IP accurately within a few tenths of an eV without any adjustable parameter. The onset of a finite cross section starts below the IP in the regime of unoccupied bound states by using an extended continuum model ansatz. This regime close to the IP and below is not important for the present results and will be discussed elsewhere. However, from the angular dependence in Fig. 1, we can distinguish between the atomic cross section $\mu_0(E)$ (bold-dotted line) and the σ^* shape resonance. It can be seen that the resonance cross section is 1 to 2 times larger than the μ_0, i.e., about 4 Mbarn at $T = 0$ K in absolute units. The present multiple scattering calculations predict the existence of a resonance for C_2H_6 in the continuum part of the spectrum. Earlier calculations [10,11] predicted the existence of a σ^* resonance of predominantly C-H character below the threshold. However, we obtain here a resonance maximum for C_2H_6 close but above the IP [Fig. 1(a)]. The present results are supported by angular dependent NEXAFS measurements of oriented C_2H_6 molecules on Cu(100) [7,8]. A resonance of σ symmetry is identified above the threshold in this case, indicating that this feature possesses mostly C-C character. Here, an isolated feature of C-H character is not identified.

One purpose of our study is to verify that the σ^* shape resonance can be accurately described by calculating multiple scattering effects of the excited photoelectron between the C atoms of the hydrocarbon molecule. It is therefore expected that the properties of this quasibound state will depend on intramolecular properties alone and less on neighboring atoms. In Fig. 2, the theoretical

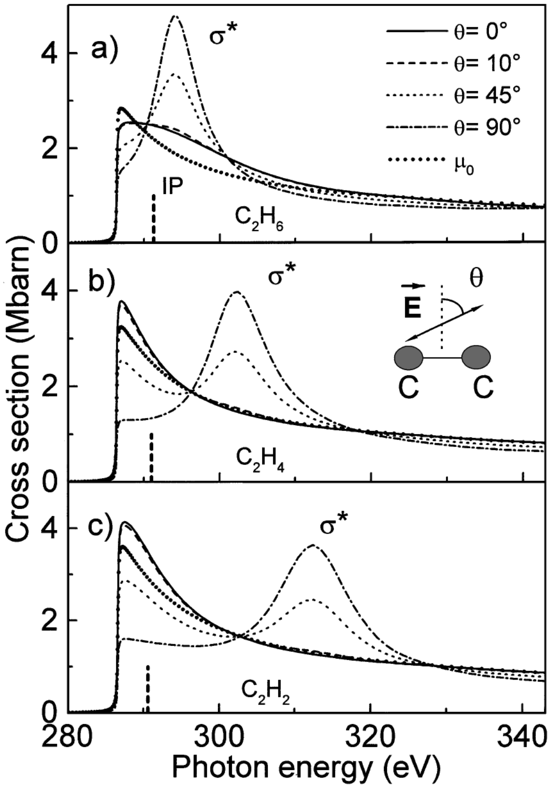

FIG. 1. Calculated C 1*s* NEXAFS spectra of C_2H_6 (a), C_2H_4 (b), and C_2H_2 (c) for different orientations of the **E** vector of the photon beam with respect to the intramolecular C-C bond. $\theta = 0°$ corresponds to a perpendicular orientation, $\theta = 90°$ to a parallel one [see inset of (b)]. Additionally to the angular dependence, the energy position of the σ^* shape resonance is changing depending on the C-C bond length of the hydrocarbon molecule. The atomic background $\mu_0(E)$ is indicated by the bold-dotted line. The vertical dashed lines represent the calculated IP.

TABLE I. Columns 1 and 2 show the experimental and calculated IP for the gas-phase molecules. The maximum positions E_{max} of the σ^* shape resonances observed in the experimental spectra and in our calculations are also given, both for the gas phase and adsorbed on Cu(100).

	IP_{exp} [eV]	IP_{theo} [eV]	$E_{\mathrm{max,exp}}$	$E_{\mathrm{max,theo}}$	$E_{\mathrm{max,exp}}$	$E_{\mathrm{max,theo}}$
			Gas phase [eV]		Cu(100) [eV]	
C_2H_6	290.7	291.3	291.2	294.1	291.4	292.0
					almost physisorbed	
C_2H_4	290.8	291.0	301.0	301.8	299.5	299.4
					chemisorbed	
					296.5	296.6
C_2H_2	291.1	290.6	310.0	311.6	298.6	298.5
Reference	[20]	this work	[3]	this work	[9], this work	this work

spectra are shown for three different "chemical environments" of the C-C bond in C_2H_4. The calculations are performed for two different $d_{\mathrm{C\text{-}C}}$. The value 1.337 Å corresponds to the gas-phase bond length of ethylene, and 1.45 Å is the value for the molecule chemisorbed on the Cu(100) surface [7]. The solid lines show the calculations of an artificial C_2 molecule without H atoms, while the dashed lines represent the calculations for an ethylene molecule, and the dotted ones for a C_2H_4 molecule adsorbed flat on a Cu(100) surface [9]. In both calculated sets in Figs. 2(a) and 2(b), no remarkable changes of the shape and the position of the resonances in the spectra, caused by the modification of the chemical environment, can be noticed. But, as already described in Fig. 1, the resonance shifts to lower energy for the stretched C-C bond.

A relationship between $d_{\mathrm{C\text{-}C}}$ in the hydrocarbons and E_{max} was also found for the molecules adsorbed on different metal surfaces. We have measured the NEXAFS spectra of ethylene, chemisorbed and physisorbed on a Cu(100) surface, for normal (90°) and grazing x-ray incidence (20°). The C K-edge NEXAFS spectra of submonolayer coverages of ethylene adsorbed on a Cu(100) single crystal were recorded at the new BESSY-II facility. The angular dependence of the observed molecular π^* and σ^* shape resonances can be seen in Fig. 3(a), where we have plotted the difference spectra $\mu(90°)$-$\mu(20°)$ for C_2H_4. Here we will not discuss the π^* resonance at 285 eV and the C-H resonances around 289 eV. Because of the larger intensity of the σ^* shape resonance for 90° as compared to 20° and vice versa for the π^* resonance, the molecules were deduced to lie flat on the Cu surface. For the chemisorbed species, the shape resonance peak is at lower energy as compared to the physisorbed case, indicating a stretching of the intramolecular bond. This stretching can be explained by a charge transfer from the Cu surface into the antibonding π^* orbital of ethylene and, hence, the weakening of the C-C bond [21]. From Fig. 3(a), we obtain $E_{\mathrm{max}} = 299.5$ and 296.5 eV, for the physisorbed and the chemisorbed species, respectively. The shift of 1.5 eV of the resonance with respect to the gas phase (dashed line) illustrates that C_2H_4 is weakly bonded and almost physisorbed. The displacement is larger for the chemisorbed phase (4.5 eV), showing a stronger interaction with the substrate. In Fig. 3(b), we show calculations for both cases, together with the corresponding experimental data for 90°. In the experiment, the atomic positions vary slightly due to thermal vibrations and disorder. In order to take this into account in our calculations, we introduced Debye-Waller damping. Given the fact that FEFF8 uses the FMS approach, the treatment of disorder in terms of Debye-Waller factors is only approximate. Using FEFF8 without FMS, i.e., using the path expansion, we estimate a value of $\sigma^2 \sim 0.0036$ Å^2 for single scattering. This value may appear high, but in a recent work [15] it was found that the intramolecular vibrations are

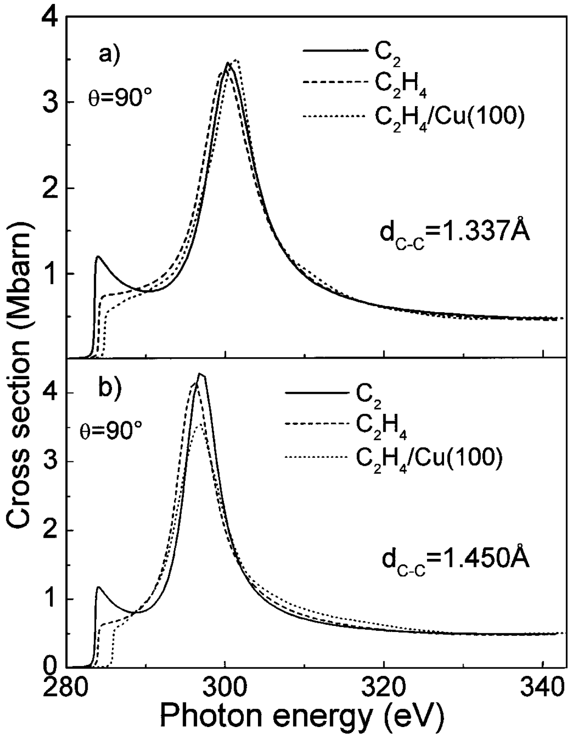

FIG. 2. (a) Calculations from an artificial C_2 molecule, an C_2H_4 molecule, and an C_2H_4 molecule adsorbed on Cu(100) for a fixed C-C bond length of 1.337 Å. (b) Corresponding calculations as in (a) using $d_{\mathrm{C\text{-}C}} = 1.450$ Å.

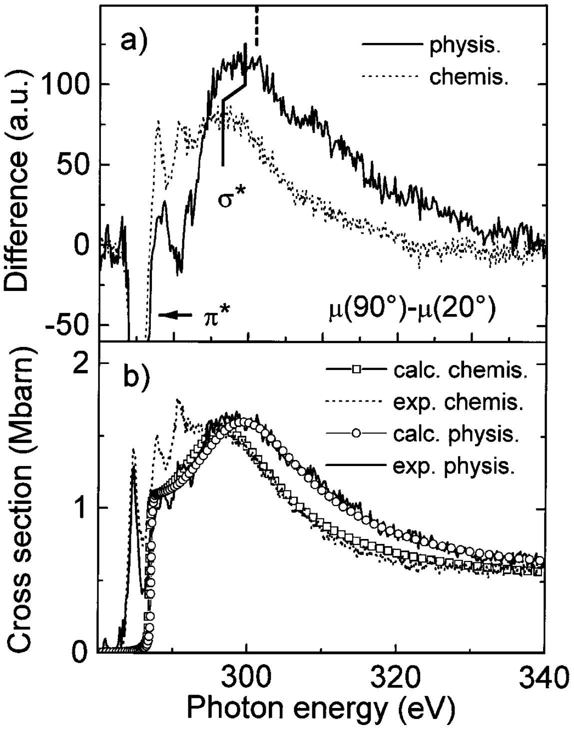

FIG. 3. (a) Difference spectra μ(90°)-μ(20°) of a submonolayer C_2H_4 on Cu(100), almost physisorbed at 26 K (solid line) and chemisorbed at 60 K (dotted line). The dashed line at the top is indicating the $E_{\max}$ for gas-phase ethylene. (b) Experimental and calculated C 1s NEXAFS spectra of C_2H_4 adsorbed on a Cu(100) surface. Both the spectra of the almost physisorbed and the chemisorbed state are shown. In experiment and theory, a shift of the σ^* shape resonance of the chemisorbed phase towards lower energy can be recognized (see Table I).

influenced by the excitation of the photoelectron into an antibonding state (σ^* shape resonance). Therefore the interpretation of the mean square relative displacement in the present analysis of the σ^* shape resonance is more complicated as compared to ground state properties. As we use only a single scaling parameter to match theory and experiment, the agreement between theory and experiment is very good. This indicates that either (i) the satellite contributions identified by Kempgens *et al.* [13,14] are negligible for physisorbed molecules, or (ii) that they do not play a role here, using angle integrated detection schemes, in contrast to Refs. [13,14].

In summary, the combination of angular dependent *ab initio* calculations with experimental NEXAFS spectra of oriented molecules gives new insight into the analysis and understanding of molecular spectroscopy, which is complementary to gas-phase spectroscopy studies. The result may also be taken as a combined (theory and experiment) case study of scattering at potential wells applied to surface science and NEXAFS. Figure 1 clearly shows a scattering cross section of 3–4 Mbarn for the σ^* shape resonance. For finite temperature this will be reduced [Fig. 3(b)], but it still remains twice as intense as the main edge jump. The advantage of today's theory is also that one can "dismount" the molecule, i.e., study the influence of the hydrogens and the metal substrate on the resonance (Fig. 2).

Discussions with A. M. Bradshaw are acknowledged. This work was supported by the BMBF (No. 05 SF8 KEA).

---

*Corresponding author.
Email address: babgroup@physik.fu-berlin.de

[1] J. L. Dehmer, D. Dill, and S. Wallace, Phys. Rev. Lett. **43**, 1005 (1979).
[2] J. Stöhr *et al.*, Phys. Rev. B **36**, 2976 (1987).
[3] F. Sette, J. Stöhr, and A. P. Hitchcook, J. Chem. Phys. **81**, 4906 (1984).
[4] M. N. Piancastelli *et al.*, J. Chem. Phys. **90**, 3004 (1989).
[5] H. Rabus *et al.*, Phys. Scr. **41**, 846 (1990).
[6] D. Arvanitis *et al.*, Phys. Rev. Lett. **57**, 3175 (1986).
[7] D. Arvanitis *et al.*, Surf. Sci. **178**, 686 (1986).
[8] D. Arvanitis *et al.*, Z. Phys. D **11**, 219 (1989).
[9] D. Arvanitis, L. Wenzel, and K. Baberschke, Phys. Rev. Lett. **59**, 2435 (1987).
[10] R. E. Farren, J. A. Sheehy, and P. W. Langhoff, Chem. Phys. Lett. **177**, 307 (1991).
[11] J. A. Sheehy, T. J. Gil, C. L. Winstead, R. E. Farren, and P. W. Langhoff, J. Chem. Phys. **91**, 1796 (1989).
[12] J. P. Connerade, *Giant Resonances in Atoms, Molecules and Solids*, edited by J. P. Connerade, J. M. Esteva, and R. C. Kartanak, NATO ASI Series (Plenum Press, New York, 1987), p. 3.
[13] B. Kempgens *et al.*, Phys. Rev. Lett. **79**, 35 (1997).
[14] B. Kempgens *et al.*, Surf. Sci. **425**, L376 (1999).
[15] S. L. Sorensen *et al.*, Phys. Rev. A **58**, 1879 (1998).
[16] T. D. Thomas *et al.*, Phys. Rev. Lett. **82**, 1120 (1999).
[17] A. L. Ankudinov *et al.*, Phys. Rev. B **58**, 7565 (1998).
[18] J. J. Rehr, J. Appl. Phys. **32**, 8 (1993).
[19] J. J. Rehr, R. C. Albers, and S. I. Zabinsky, Phys. Rev. Lett. **69**, 3397 (1992).
[20] *Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Boca Raton, 1994).
[21] J. Stöhr, *NEXAFS Spectroscopy*, Springer Series in Surface Science (Springer-Verlag, Heidelberg, 1992).
[22] J. P. Connerade, J. Phys. B **17**, L165 (1984).
[23] I. Nenner, J. Chem. Phys. **91**, 259 (1989).
[24] A. P. Hitchcook, P. Fischer, and R. McLaren, J. Chem. Phys. **91**, 281 (1989).