

π^* and σ^* Excitons in C 1s Absorption of Graphite

P. A. Brühwiler, A. J. Maxwell, C. Puglia, A. Nilsson, S. Andersson, and N. Mårtensson

Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden

(Received 27 April 1994)

We have studied the π^* and σ^* threshold structures in the C 1s x-ray absorption spectrum of graphite using core level autoionization spectroscopy. We confirm that the σ^* threshold feature is an exciton. We find that the prominent π^* feature is also excitonic, though it lies approximately 1 eV above the π^* threshold. This excited state is localized on a time scale of fs, even though it is degenerate with propagating states of the crystal.

PACS numbers: 78.70.Dm, 71.35.+z, 73.20.Dx, 73.20.Hb

Graphite is a prototypical two-dimensional material. Intraplanar sp^2 bonding leaves a singly occupied p orbital at each C atomic site, and the intraplanar π system formed from these is responsible for the semimetal character and optical properties of the solid. The weak interplanar interaction is also well known, giving graphite its utility as a lubricant. One can account for most of the properties of graphite, and indeed for many graphite compounds, by considering only a single sheet, or array of nearly independent sheets. It is therefore interesting to try to take advantage of this system in order to study electronic screening for low system dimension.

One of the main arenas for this class of problems has been the core spectroscopies: C 1s x-ray absorption (XAS) [1–3], photoelectron (XPS) [4], Auger [5], and emission (XES) [6]. Modeling of the experimental profiles has been done for all of the above: XAS [1,7], XPS [4], Auger [5], and XES [6]. All of these works have focused on excitonic aspects of the valence-electron-core-hole interaction. The most direct probes thus far have been XAS and XES studies of the unoccupied bands. The σ or π character of the bands is clear from angle-dependent XAS measurements [8]. This is illustrated in Fig. 1 as well, where we show three representative angles. The first ~ 6.5 eV of the spectrum shows π character, with a sudden onset at the σ^* threshold.

The σ^* threshold peak has been interpreted in two ways—Batson [2] discussed it in terms of the ground state density of states (DOS) calculations of Ref. [7], while Ma *et al.* [6] concluded that the σ^* threshold feature is an exciton with a binding energy on the order of several tenths of an eV, and that states above it are delocalized. The fact that the electron quasiparticle is spatially localized enough to the core-excited C atom to mutually annihilate the core hole a sizable percentage of the time [9] is indeed strong support for the Frenkel exciton description of this excitation; the excited electron occupies a highly localized one-electron state which is “pulled off” the bottom of a band gap. In this interpretation, the perfect division into π^* and σ^* prevents significant mixing of the σ^* exciton into the delocalized π^* manifold with which it is degenerate, and it is quite similar to the diamond C 1s exciton [6].

Varying conclusions have also been drawn regarding the strong excitation above the π threshold, which has no analog for sp^3 bonding systems. Mele and Ritsko [1] considered a single layer of graphite and studied it using a tight-binding Green's function approach. They found a large excitonic effect based on the shift between the singularity in the ground state DOS and the theoretical core-excited DOS necessary to simulate their XAS data.

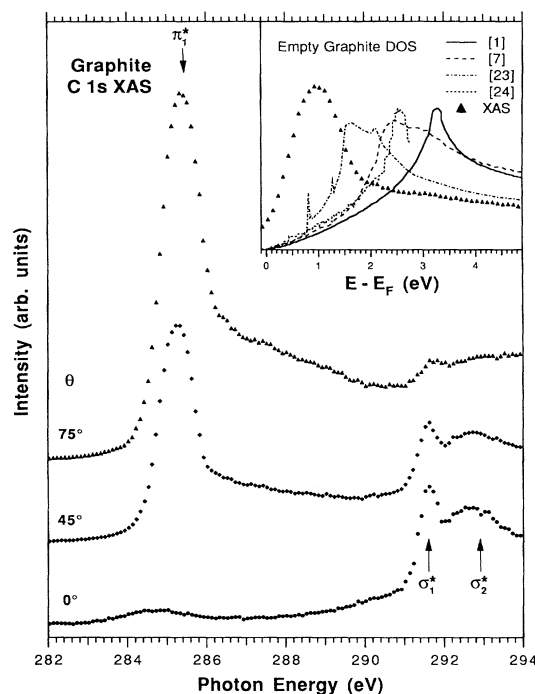


FIG. 1. XAS of HOPG graphite, with light polarized in the plane of incidence incident at the given angles with respect to normal. The dipole selection rules govern XAS, so that transitions from the 1s level go to states of p symmetry, which are distributed anisotropically as described in the text. We tentatively attribute the slight peaking in the region of the π_1^* transition for $\theta = 0^\circ$ to a combination of small local imperfections in the sample and partial circular polarization of the light. Inset: Comparison of the $\theta = 75^\circ$ spectrum to calculations from the indicated references, using the calibration described in the text.

Their calculations also indicated that the states making up the excited state DOS peak were delocalized over the graphite sheet, but resonantly enhanced at the core-excited atom. Indirect evidence for excitonic effects at the C $1s$ π threshold was subsequently claimed from XPS [4], for which the XPS shakeup profile was modeled with a sharp peak in the unoccupied DOS near E_F , in qualitative agreement with XAS. More recently, Weng, Rez, and Ma [7] contradicted the results of Ref. [1]. They concluded that their ground state DOS accurately modeled the XAS spectrum, and that excitonic effects were therefore minor; recent cluster multiple-scattering calculations support their results [10]. This conclusion was pointed out as a particular challenge to the theory of core excitations in π systems [11]. Batson supported the assignment of Weng, Rez, and Ma using a model in which a small excitonic enhancement was applied to their calculated ground state DOS [2] to fit his data, and implied that the results of Ref. [1] suffered from the two-dimensional model used. Thus, recent work suggests that there is virtually no excitonic effect in the screening of a C $1s$ hole by either the π or σ bands in the infinite two-dimensional system.

Another experimental approach to this problem, related to those above, is core level autoionization. One can, e.g., excite C $1s$ electrons to near-threshold XAS excited states with monochromatic synchrotron radiation, and monitor the decay of the chosen excited state via electrons which are emitted. Auger-like processes account for $\sim 99\%$ of that decay and, for total localization of the excited state to the vicinity of the core hole (as in isolated molecules), can be divided into final states with one valence hole quasiparticle, or one conduction electron and two valence hole quasiparticles. In single-particle terms, these correspond to core-hole-decay channels in which the excited $1s$ electron is involved ("participator autoionization") or not ("spectator autoionization") [12], respectively. Participator autoionization gives a strong signature for the primary π^* transitions in graphite "models" such as benzene [13] and C_{60} [14]. These molecules have band gaps which allow an excited state to be pulled off a given band and localized to the hole, in the sense of a Frenkel exciton [15,16]. Thus, the participator channel is proof of a localized and long-lived level in the XAS final state. Spectator autoionization gives similar information on excited state localization, via the appearance of Auger (two-hole) transitions at elevated kinetic energies, due to the localized screening effect of the spectator electron.

In this Letter, we present C $1s$ autoionization measurements of the prominent graphite XAS excited states and find a strong participator contribution at the σ^* threshold, thus confirming the XES results on the σ^* exciton. 1 eV above threshold, at the next σ^* transition, the spectrum resembles normal Auger, proving that this transition places the excited $1s$ electron into a propagating state. 1 eV

above the π^* threshold, on the other hand, our results show unequivocally that *there is a considerable localization of the intense π^* excitation, even though there is no band gap to sustain it as a true exciton.*

The data were taken at beam line 22 at MAX-Lab in Lund [17], which consists of a modified SX700-II monochromator and a 200 mm hemispherical electron energy analyzer of Scienta type, built in Uppsala. The sample was highly oriented pyrolytic graphite (HOPG) and was cleaved in air immediately prior to mounting and chamber pumpdown. We cleaned the sample by heating to $\sim 900^\circ\text{C}$. All electron spectra presented here were taken with photon energy resolution of 0.3 eV, and electron energy resolution of 0.6 eV. The electron emission angle was 45° from normal for normal-incidence (σ^*) excitation and 30° from normal for grazing-incidence (π^*) excitation. Auger spectra excited by 350 eV photons and taken with these settings were virtually indistinguishable in shape, ruling out any unwanted angular effects in the data.

In Fig. 1 we show the XAS of our sample taken with 0.13 eV photon energy resolution, as a function of the polar angle of the incoming radiation with respect to the graphite planes. These data compare well with other recent data [2,6]. In particular, the sharp σ^* exciton is well resolved, marked by σ_1^* in the figure. Figure 2 shows the C $1s$ autoionization spectra for excitations σ_1^* and σ_2^* , as well as the Auger spectrum, on the kinetic energy scale.

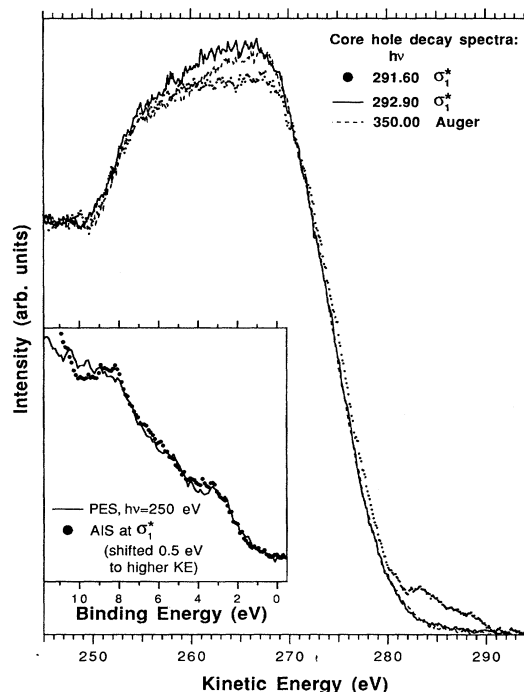


FIG. 2. Core hole decay spectra at the indicated excitations. Inset: High kinetic energy structure from σ_1^* autoionization vs photoemission excited by 250 eV light, taken at the same emission angle.

Directly apparent is an extra feature in the σ_1^* autoionization spectrum which vanishes at the σ_2^* excitation. The inset shows this feature vs photoemission data taken at $h\nu = 250$ eV. The latter comparison indicates a common origin for those spectra as single-hole final states, i.e., the extra feature is due to participator autoionization. This is further clarified by its absence in the σ_2^* autoionization. An additional important detail is the -0.5 ± 0.2 eV binding energy shift required to achieve a reasonable match between the σ_1^* autoionization and valence data, which is just the Stokes shift determined previously [6]. Thus, we confirm the assignment of Ma *et al.* [6]. The lack of participator autoionization shows at the same time that the σ_2^* excitation is extremely delocalized [18], and indeed the resulting deexcitation spectrum is only slightly different from the Auger.

We compare the π_1^* autoionization spectrum to the Auger data in Fig. 3 on a kinetic energy scale [19]. These data show a strong alteration of the line profile near the spectral maximum relative to the Auger, as well as significant new intensity along the leading edge. Taking difference spectra by matching the data at high and low energies with the Auger, we compare them to the valence photoemission data. The leading edges match very well [20], suggesting a likely contribution from participator autoionization for the π_1^* excitation. The small shoulder at 283 eV in the full spectrum corroborates this assignment, since it is not possible to explain this as part of a shifted Auger spectrum expected for spectator

autoionization. However, the single-peak shape of the dominant portion of the resonant spectrum differs from the double peaking observed for the σ_1^* deexcitation and photoemission data, indicating other contributions must also be present. If slightly less Auger background were subtracted, this portion of the spectrum would resemble the Auger, so that it is most simply explained as due to spectator autoionization. The relative importance of participator and spectator autoionization in the spectrum cannot be addressed at this point. In any case, *both contributions constitute unambiguous experimental proof that the π_1^* excitation is localized on a time scale comparable to the core-hole lifetime* [21].

From the excited state localization reported here, it is clear that a ground state DOS fails in describing the physics in a fundamental way, contrary to the conclusions of Refs. [2,7,10]. Regarding the *shape* of the unoccupied DOS, previous questions can be traced to problems in alignment of theory and XAS data, which requires locating E_F in the data. E_F for XAS is given by the C 1s binding energy [22], since this is a system with a continuous distribution of states around E_F . After many measurements at Lund and an XPS system in Uppsala, we find a graphite C 1s binding energy of 284.4 ± 0.1 eV. This is in excellent agreement with the theory-derived threshold energy found by Mele and Ritsko [1]. Comparing unoccupied graphite DOS calculations in the literature, the singularity associated with the Q_{2g}^- critical point in the ground state is located at 1.5 eV [23], 2.3 eV [7,24], and 3.2 eV [1] above E_F [25]. The peak in the XAS data which is associated [1,2,7] with that singularity occurs 1.05 ± 0.10 eV above E_F , implying an "excitonic shift" of 0.5 to 2.2 eV, or $>30\%$ [26]. This is shown in the inset of Fig. 1 and qualitatively confirms the analysis of Ref. [1].

The *physical localization* of the excited electron quasiparticle has not been discussed in the theoretical work. It is an effect outside that usually considered for the core exciton problem in three-dimensional metals, which has typically been treated within the Mahan-Nozières-De Dominicis (MND) model [27]. In the latter model, each quasiparticle is weakly perturbed by the localized core hole, and the scattering of all conduction electrons from the core-hole potential provides the screening charge density. The kinetic energy of a quasiparticle at $E_F + 1$ eV should be sufficient in this picture to remove it rapidly on the scale of the core-hole lifetime, and the strongest excitonic effects occur *right at E_F* , where the lowest energy screening excitations occur. On the other hand, if one starts with the $Z + 1$ analog, in which the core-excited C atom is considered as a N impurity, the impurity site is also expected to be almost completely screened [28]. Interestingly, much of the screening is derived from alterations in the σ bands, as well as the π bands, for the neutral ground state. In this more chemical picture, the π_1^* resonance would correspond to an analog of an impurity

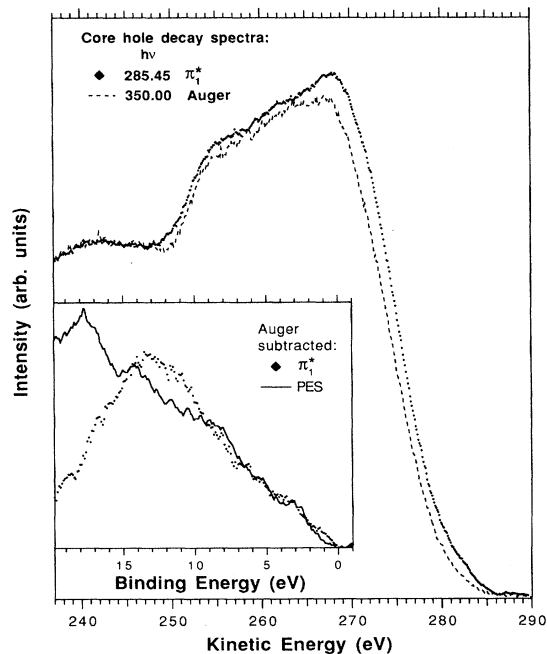


FIG. 3. Core-hole decay spectra at the indicated excitations. Inset: The π_1^* decay spectrum, after subtracting the Auger as described in the text, vs 250 eV photoemission data.

donor level in a semiconductor, and the dominant contribution to its width would be its lifetime (i.e., its hopping bandwidth). Taking the width to be ~ 1 eV, this implies a participator autoionization contribution of $\sim 2\%$ to the total decay spectrum [29], which is empirically of the correct order of magnitude (see Fig. 3). From the solid state perspective, the π_1^* excitation is unique in that, instead of being pulled off the bottom of a band as is the σ_1^* state, it is derived from a band inflection point located several eV above E_F , which in principle provides significant phase space for decay of the excited electron quasiparticle into lower energy states. This is indeed what occurs in *sp* metals, for which to our knowledge the electron decay spectrum never deviates with varying excitation energy from the Auger.

The autoionization found at π_1^* is furthermore a direct contradiction of the analysis of Houston *et al.* [5], who also attempted to measure this effect. Their model of an excited state DOS with a singularity right at E_F is also seen to be physically unrealistic. The spatial excited state localization found by us suggests that further theoretical analysis of all aspects of the screening of a C $1s$ core hole in graphite [1,4,5] is necessary to reconcile these phenomena with accepted models such as MND [27,30] and to connect that framework with the “chemical picture” of core excitations.

To summarize, we have confirmed the most recent assignment of the σ^* core exciton in graphite [6] and found that the band immediately above it is well delocalized. The problem of the excitonic effect on the π^* DOS with C $1s$ excitation has been clarified and shown to hold semiquantitatively to the original proposition of Mele and Ritsko [1]. We prove that the latter excitation is localized on a time scale of fs to the core-hole site, which is not yet explained by present theories for core excitations in graphite [1] or three-dimensional metals [27], and which appears to represent a new class of core exciton.

We wish to acknowledge stimulating discussions with Y. Ma and D.C. Mancini, and P. Glans, A.W. Moore and R.E. Palmer for providing the graphite sample, and funding by the Swedish Natural Science Research Council (NFR).

-
- [1] E. J. Mele and J. J. Ritsko, Phys. Rev. Lett. **43**, 68 (1979).
 - [2] P. E. Batson, Phys. Rev. B **48**, 2608 (1993).
 - [3] References [1] and [2] used transmission electron energy loss spectroscopy, but in conditions of low transverse-momentum transfer, such that the spectrum is equivalent to x-ray absorption data.
 - [4] P. M. T. M. van Attekum and G. K. Wertheim, Phys. Rev. Lett. **43**, 1896 (1979).
 - [5] J. E. Houston *et al.*, Phys. Rev. Lett. **56**, 1302 (1986); Phys. Rev. B **34**, 1215 (1986).
 - [6] Y. Ma *et al.*, Phys. Rev. Lett. **71**, 3725 (1993).
 - [7] X. Weng, P. Rez, and H. Ma, Phys. Rev. B **40**, 4175 (1989).

- [8] R. A. Rosenberg, P. J. Love, and V. Rehn, Phys. Rev. B **33**, 4034 (1986).
- [9] As seen from the exciton intensity in XES [6].
- [10] Y. Zou and J. C. Tang, J. Phys. Condens. Matter **6**, 2949 (1994).
- [11] J. Stöhr, *NEXAFS Spectroscopy* (Springer-Verlag, Berlin, 1992), p. 206.
- [12] O. Björneholm *et al.*, Phys. Scr. **T41**, 217 (1992).
- [13] D. Menzel *et al.*, J. Chem. Phys. **96**, 1724 (1992).
- [14] P. A. Brühwiler *et al.*, Chem. Phys. Lett. **193**, 311 (1992).
- [15] R. S. Knox, *Theory of Excitons, Solid State Physics Supplement 5* (Academic, London, 1963).
- [16] B. Wästberg *et al.*, Phys. Rev. B **50**, 13031 (1994), calculated this effect for C₆₀.
- [17] J. N. Andersen *et al.*, Synchrotron Rad. News **4**, 15 (1991).
- [18] P. A. Brühwiler *et al.*, Phys. Rev. Lett. **71**, 3721 (1993).
- [19] For the former, it was necessary to subtract the C $1s$ line excited by second-order light, which was done by taking a first-order spectrum over a wide energy range and matching it to that extrinsic feature; no noticeable changes resulted in the spectral structure we discuss.
- [20] Fine structure in the single-hole decay may be washed out due to the nonzero hopping matrix element in the intermediate state, as observed, e.g., for the participator decay at the second π^* excitation of C₆₀ [18].
- [21] About 6 fs, based on gas phase measurements of the lifetime of C $1s$ holes for ionized and core-excited molecules, corresponding to minimal and maximal valence electron density at the core-hole site, respectively; see [18] and references therein for more details.
- [22] A. Nilsson *et al.*, Chem. Phys. Lett. **197**, 12 (1992).
- [23] R. Ahuja *et al.* (to be published).
- [24] B. R. Weinberger *et al.*, Phys. Rev. Lett. **41**, 1417 (1978).
- [25] One should in principle compare to a quasiparticle calculation, which for a graphite monolayer has been carried out by M. Vracko, C.-M. Liegener, and J. Ladik, Chem. Phys. Lett. **153**, 166 (1988); they find that shifts of $\sim 20\%$ to lower or higher energy can occur for different unoccupied bands; see also Ref. [26].
- [26] Reference [1] states that the kink in the XAS data at 1.9 ± 0.1 eV marks the DOS singularity of the ground state, giving a 44% excitonic shift, and consistent with the most recent calculations of the graphite DOS [23].
- [27] K. Ohtaka and Y. Tanabe, Rev. Mod. Phys. **62**, 929 (1990).
- [28] C. Pisani, R. Dovesi, and P. Carosso, Phys. Rev. B **20**, 5345 (1979).
- [29] We estimate this number starting with a 20% contribution from the excited electron, assuming it to be totally localized to the excited atom, and take 10% of that due to the ratio of hopping bandwidth to core lifetime broadening [18]. Aside from the question of relative Auger matrix elements among the different final states, there is the issue of localization of unoccupied levels and delocalization of occupied ones upon core excitation [30], which would enhance the contribution under consideration.
- [30] C. Enkvist *et al.*, Phys. Rev. B **48**, 14629 (1993), showed such corrections are suggested by C₆₀ $1s$ XPS data.