peak.

In summary, four major conclusions are reported in this Letter. (1) In conjunction with a theoretical calculation of the $\vec{k}_{\parallel}$-resolved SLDS, the edge proximity effects, which result from the dispersion of the resonances, have provided experimental evidence for the band-structure effects in FEED.[13,15] (2) The present theoretical model calculation of the $\vec{k}_{\parallel}$-resolved SLDS has been shown to be successful in explaining the observations in both FEED and angle-resolved PED. (3) This FEED study on Mo(100) confirms the existence of surface resonances and also reveals their dispersive characteristics. Published results for angle-resolved PED from Mo(100)[11] do not definitely demonstrate the existence of a surface resonance peak.[19] (4) The present calculation shows that the resonance on (100) surfaces of Mo and W are mainly made up of d_{zx}, $d_{x^2-y^2}$, and s orbitals. Each resonance is located in a hybridization gap which, when traced back to the bulk band structure at $\vec{k}_{\parallel}=0$, is found to be related to the crossover of Δ_2 and Δ_5 bands.

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[19] S. L. Weng and E. W. Plummer, to be published. Recent angle-resolved as well as angle-integrated PED measurements on Mo(100) in our own laboratory at 16.8 and 21.2 eV clearly show the existence of this resonance peak.

Electron–Molecular-Vibration Coupling in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)

M. J. Rice and N. O. Lipari
Xerox Webster Research Center, Webster, New York 14580

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We comment on the feasibility of a recent suggestion by Carneiro that the Kohn anomaly in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) occurs in the C-H stretch molecular modes.

In a recent Letter discussing the inelastic-neutron-scattering studies[1,2] of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), Carneiro[3] has made the interesting point that the inelastic-neutron-scattering intensities from protonated TTF-TCNQ and deuterated TTF-TCNQ (D) can be quite different for particular molecular-vibrational modes. His suggestion that the Kohn anomaly and related Peierls distortion in TTF-TCNQ arises *specifically* from the coupling of the conduction electrons to C-H or C-D molecular-vibrational modes should not, however, be considered without cognizance of some recent results pertaining to the role of electron–molecular-vibration coupling in this type of organic conductor.

Molecular-orbital (MO) and valence-force-field calculations of the linear coupling constants describing the interaction of the relevant conduction electron MO's with the totally symmetric (a_g) molecular vibrations of the TCNQ[4] and TTF[5] molecules show that there is almost *negligible* coupling to the C-H (or C-D) stretch modes. The results of these calculations are summarized in Table I for the protonated molecules. This conclusion has been reached earlier[6] for the TCNQ molecule on the basis of the elementary observation that the C-H (or C-D) stretch mode involves atomic displacements in regions of the molecule where the amplitude of the relevant MO $[b_{2g}(\pi^*)]$ is very small. In either molecule, the MO's couple linearly only to the totally symmetric (a_g) vibrational modes; there are ten a_g modes for the TCNQ molecule[7] and seven for the TTF molecule.[8] The linear electron–molecular-vibration coupling constants g_n are defined such that in the formalism of second quantization the Hamiltonian specifying the electron–molecular-vibration interaction is[9,6,4]

$$H = C^\dagger C \sum\nolimits_n g_n \hbar\omega_n (b_n^\dagger + b_n),$$

where $b_n^\dagger$ is the creation operator for the nth vibration quantum mode of frequency ω_n and $C^\dagger$ is the electron creation operator for the MO. The quantity $E_p = \hbar \sum_n g_n^2 \omega_n$, which is the "small-polaron" binding energy, serves as a relative measure of the total electron–molecular-vibration coupling strength; the respective values of E_p for the TCNQ and TTF molecules are included in Table I.

It is evident from Table I that the conduction electrons in TTF-TCNQ are significantly coupled to a relatively large number of intramolecular vibrational modes. As discussed in some detail by Rice, Duke, and Lipari,[6] this implies that the subsequent soft phonon forming the Kohn anomaly will consist of a *strong mixing of all of these modes*—together with any other modes, e.g., acoustic phonon modes, which happen to couple to the underlying conduction-electron MO. Consequently, it is not possible to associate the soft phonon and the subsequent Peierls distortion with a *single* originally uncoupled phonon or vibrational mode. It is this interesting complication of multicouplings that distinquishes TTF-TCNQ

TABLE I: Calculated linear electron–molecular-vibration coupling constants for the lowest empty molecular orbital $[b_{2g}(\pi^*)]$ of TCNQ and the highest occupied molecular orbital $[b_{1u}(\pi)]$ of TTF.

TCNQ			TTF		
a_g frequency[a] (cm^{-1})	Domanant[a] character	Coupling constant	a_g frequency[b] (cm^{-1})	Dominant[b] character	Coupling constant
3048	C-H stretch	0.01	3099	C-H stretch	0.03
2229	C≡N stretch	0.19	1559	C-C stretch center C-C stretch ring	0.23
1602	C=C ring stretch C-H bend	0.66	1518	C-C stretch center C-C stretch ring	0.62
1454	C=C wing stretch	0.27	1077	S-C-H bend	0.16
1207	C-H bend C=C ring stretch	0.19	740	S-C stretch	0.49
948	C-C ring stretch	0.25	472	C-S stretch C-S-C bend	1.33
711	C-C ring stretch	0.37	253	S-C-S bend C-S-C bend	0.16
602	$C(CN)_2$ scissor C-C wing deformation	0.03	Corresponding small polaron binding energies $E_p = \hbar \sum_n g_n^2 \omega_n$.		
334	ring deformation	0.58	TCNQ	TTF	
144	C-C≡N bending	0.49	0.15 eV	0.21 eV	

[a] After Girlando and Pecile, Ref. 7.

[b] After Bozio *et al.*, Ref. 8.

from $K_2[Pt(CN)_4]Br_{0.3}\cdot 3.2H_2O$ (KCP).[10]

Direct experimental information on both the existence and magnitudes of electron-phonon or electron-vibrational couplings in organic linear chain conductors can be obtained because in the Peierls condensed state, or, more generally, in a band semiconducting state, the phonon modes which are coupled to the conduction electrons develop, as a consequence of their coupling, an anomalous infrared activity along the chain direction.[11] A recent analysis[12] of this effect in triethyl ammonium-$(TCNQ)_2$, for which excellent polarized optical reflectance data exist,[13] has verified that the TCNQ conduction electrons significantly couple to all of the symmetric TCNQ vibrational modes excepting the C-H stretch mode. Moreover, the experimental values which were deduced[12] for the respective coupling constants are in good semiquantitative agreement with the theoretical values tabulated in Table I. Similar conclusions may also be drawn from a recent polarized reflectance study of K-TCNQ.[14] The presently available infrared data[15] on TTF-TCNQ show no evidence of any appreciable electronic coupling to either the TCNQ or TTF C-H stretch molecular modes, although there is clear evidence for electronic coupling to the 1602-cm^{-1} TCNQ a_g mode, for which, interestingly, Table I indicates strong coupling.

We do not discount Carneiro's suggestion that important differences in inelastic-neutron-scattering intensities for protonated and deuterated TTF-TCNQ may arise for particular TTF and TCNQ molecular modes. It is possible that application of his arguments to the particular linear combination of molecular modes theoretically expected[6] to participate in the Kohn anomaly may explain the differences in the observed[1,2] neutron-scattering intensities. Indeed, the majority of the TCNQ and TTF modes collected in Table I will involve some degree of protonic motion. This feature is not reflected by the dominant character specifications given in Table I since the latter, by convention, are based on the potential energies of deformation. Only in the three lowest-frequency TCNQ a_g modes and in the TCNQ $C\equiv N$ stretch mode is protonic motion absent. His suggestion that the Kohn anomaly in TTF-TCNQ is associated *specifically* with the C-H (or C-D) molecular mode does not, however, seem feasible in view of the considerations that we have outlined above.

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