Observation of Electric Monopole Transitions in Tetracyanoquinodimethane

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(Received 14 August 1975)

The first direct observation of electric monopole transitions in solids is reported for tetracyanoquinodimethane using an inelastic electron scattering experiment. Good agreement is obtained with a semiempirical self-consistent molecular-orbital calculation which predicts dipole allowed transitions near 3 and 7 eV and optically forbidden monopole transitions near 5 eV. We find an anomalous momentum dependence in the shape of the first dipole transition, possible due to local field effects.

High-energy inelastic electron scattering has long been considered a useful supplement to optical spectroscopy since with a single spectrometer one can obtain the dielectric response function over a range of energies extending from the infrared to the soft x-ray region.[1] However, with the exception of extensive measurements of plasmon dispersion,[2] comparatively little use has been made of the ability to transfer momentum in the scattering event in solid-state studies. Momentum transfer produces nonvertical transitions between energy bands and gives rise to new selection rules which greatly expand the information available through optical spectroscopy. In low-energy electron scattering experiments optically forbidden transitions have been observed for atoms and simple molecules in the gas phase,[3,4] but in solids they are only observed through the apparent breakdown of selection rules at some suitably low energy.[5]

In this paper we report results of a high-energy electron scattering experiment which yields unambiguous identification of monopole transitions in solid tetracyanoquinodimethane (TCNQ) as well as an anomalous momentum dependence of the first dipole transition possibly due to local field effects.

Within the Born approximation the differential scattering cross section per unit energy loss per unit solid angle for high-energy electron scattering is[6]

$$\frac{d^2\sigma}{dE\,d\Omega} \sim q^{-4}\textstyle\sum_f |\langle\Psi_f|e^{i\vec{q}\cdot\vec{r}}|\Psi_0\rangle|^2\delta(E_f-E_0-E),$$

where Ψ_0 and Ψ_f are the initial- and final-state wave functions with energies E_0 and E_f, respectively, and q is the momentum transferred in the inelastic event. For $q<1/r_c$ (where r_c is a characteristic size of the wave function) one can write the exponential $e^{i\vec{q}\cdot\vec{r}}\sim 1+i\vec{q}\cdot\vec{r}+\frac{1}{2}(i\vec{q}\cdot\vec{r})^2$. The first term does not contribute because of the orthogonality of initial and final states, while the second term, which dominates at very small q, contributes only dipole-allowed transitions. In terms of spherical harmonics the third term contains Y_0 and Y_2 causing both monopole and quadrupole transitions. Thus, for dipole-allowed transitions the energy-loss probability is proportional to q^{-2}, whereas it is constant for monopole and quadrupole transitions. In general, the monopole and dipole terms will be comparable when $qr_c\sim 1$ which for large molecular wave functions ($r_c\sim 2$ Å) implies $q\sim 0.5$ Å^{-1}.

A great deal of interest has been shown in charge-transfer salts based on the molecule TCNQ. While numerous calculations have been performed on the molecular orbitals of neutral and charged molecules[7] only one measured peak[8] in the optical absorption spectrum of the neutral molecule has been available to test the predicted excitations of calculated molecular orbitals. An inelastic electron scattering experiment allows the measurement of high-energy optically allowed transitions as well as optically forbidden transitions.

The results of an inelastic electron scattering experiment performed on 1500-Å-thick self-supporting polycrystalline films of TCNQ are given in Fig. 1. The spectrometer previously described[9] was operated with an energy-loss resolution of 0.1 eV and a momentum-transfer resolution of 0.15 Å^{-1}. For small values of momentum transfer we find two large peaks due to dipole transitions. The lowest peak at 3.8 eV is quite asym-

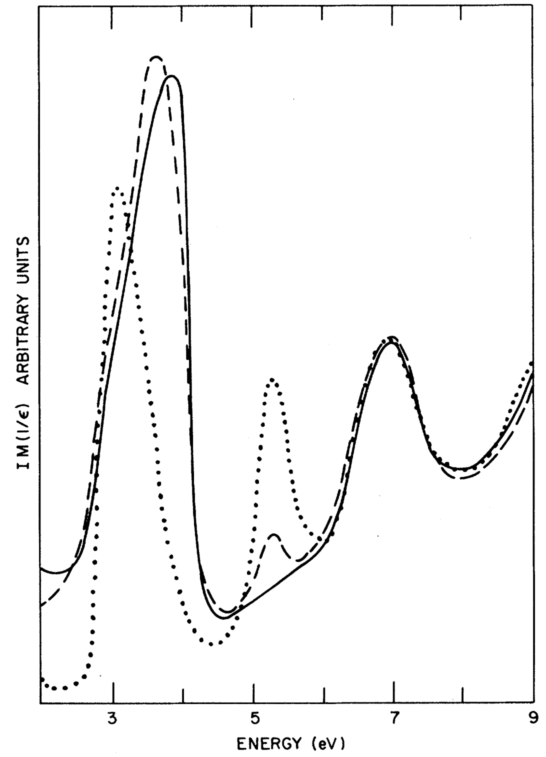

FIG. 1. Energy-loss spectra for various values of momentum transfer, q, normalized to 7-eV peak: solid line, $q = 0.13$ Å^{-1}; dashed line, $q = 0.28$ Å^{-1}; dotted line, $q = 0.56$ Å^{-1}.

TABLE I. Molecular-orbital results for TCNQ: column 1, the highest three occupied and lowest three empty molecular orbitals; column 2, the transition energies (in eV) obtained using a 3×3 CI calculation; column 3, transition symmetries; column 4, dipole-allowed oscillator strengths (in Å^{-2}).

	Transitions		
Orbital eigenvalues	Energy	Symmetry	Oscillator strength
Empty			
-1.47 a_{1u} (π)	3.40	B_{3u}	1.73
-1.50 b_{1u} (π)	4.31	B_{1g}	⋯
-4.06 b_{2g} (π)	4.85	B_{1g}	⋯
	4.94	A_{1g}	⋯
Occupied			
-9.57 b_{1u} (π)	5.56	A_{1g}	⋯
-11.79 b_{2g} (π)	6.52	B_{2u}	0.04
-11.99 b_{3g} (π)	7.19	B_{3u}	0.98
	7.27	B_{2u}	0.36
	7.85	B_{3u}	0.07

metric with a sharp high-energy edge and a full width at half-maximum of ~1.2 eV. This can be identified with the one previously observed transition[8] shown in the results of our molecular-orbital calculations in Table I as B_{3u} with energy 3.4 eV. In the vapor this single electronic transition has a large width as a result of Franck-Condon vibrational broadening, but increased broadening is observed in the solid.[10] Best agreement with the experimental line shape was obtained with a recent theory of molecular polaritons.[10,11] The second equally broad band which peaks at 7.0 eV contains contributions from two B_{2u} and two B_{3u} transitions as shown in Table I but the strength is mainly concentrated in the transitions calculated at ~7.2 eV.

The most dramatic result is the growth of the peak at 5.3 eV as the momentum transfer is increased. Relative to the dipole transitions in the 7-eV peak the strength of the 5.3-eV peak grows quadratically with q, identifying it as either a monopole or a quadrupole transition. Monopole transitions (symmetry A_{1g}) were calculated to occur at 4.94 and 5.56 eV and our observed peak is probably a composite of these two.

The electronic structure calculations for TCNQ reported here were performed using the complete neglect of differential overlap (CNDO) approximation.[12] It is well known that the version CNDO/2, while giving a good charge-density description, fails to describe the energy of the electronic states properly. Very recently,[13] a new parametrization of the CNDO method for benzene-based molecules has been developed. The new parametrization, for carbon and hydrogen, differs from the earlier ones[14] by virtue of large orbital exponents for the carbon atoms, differing core-Hamiltonian matrix elements for s and p orbitals, and the use of the Mataga-Nishimoto[15] formula for two-center Coulomb integrals. For TCNQ, we have determined the nitrogen parameters, which are somewhat different from those previously reported in the literature,[12] from the analysis of the photoemission spectra of the azines (a full description of the parametrization, results, and comparison with photoemission experiments for TCNQ will be given elsewhere). The transition energies reported here were calculated using a configuration interaction (CI) program based on an analysis like that given by Lowitz.[16] The charge densities in the CNDO ground-state calculations were made to be self-consistent to within one part in 10^3. The resulting orbital eigenfunctions and eigenvalues were used as input to the CI analysis. Following a study of the dependence of the CI prediction on the number of orbital states taken in the initial manifold, we decided that a 3×3 CI was sufficient for the description of the experimental data. The results are given in Table I. The highest three occupied and the lowest three empty molecular orbitals are given. The symmetry labeling is that of the group D_{2h} with the x axis taken to lie along the long axis and the z axis perpendicular to the plane of the molecule. The results of the CI calculation are also shown. It is to be noted that the calculated transition energies are in fairly good agreement with the results of Lowitz.[16] This is not surprising since these lowest transitions are $\pi\rightarrow\pi^*$ transitions and are little affected by the σ interactions which were neglected by Lowitz and which are important to account for the photoemission spectrum properly. More recently, Herman and Batra[17] have also calculated the electronic structure of TCNQ using the $X\alpha$ method. This calculation, while giving the same ordering for the lowest empty and highest occupied molecular orbitals, differs from ours in the position of the remaining states. Unfortunately, they calculate only the lowest singlet transition energy (2.5 eV) and therefore their model has yet to be tested on the higher singlet transitions while ours gives simultaneously a good description of the data presented here and of the photoemission spectrum of TCNQ. They do calculate the lowest singlet-triplet transition (1.7 eV) which can be measured by electron scattering, but was not seen in our experiment because of the small probability of electron exchange at the incident energy of 300 keV.[3]

A completely unexpected result in our experiment was the momentum dependence of the line shape of the first dipole transition which narrows to about 0.8 eV and changes shape to a sharp low-energy edge with a high-energy tail as momentum is increased. Since in isolated molecules Franck-Condon vibrational sidebands have no momentum-transfer dependence,[18] this shape change must be due to a solid-state effect. Energy bandwidths[19] are too narrow to produce this effect. Since the optical reflectivity line shape is best described by molecular polariton theory,[10,11] an extension of this theory to finite momentum may explain the shape change. A final possibility is a simpler calculation of local-field effects in a point-dipole model which has been used to interpret changes in energy-loss spectra as a function of momentum transfer,[20] and which should be particularly applicable to this strong transition between well-localized states.

In making a more precise comparison between theory and experiment several additional points should be considered. With the exception of the line shape mentioned above we have regarded solid TCNQ as a molecular crystal in which interactions between neighboring molecules are neglected. That this is reasonable is seen by the agreement between calculated molecular transition energies and measured values. Nevertheless, factor group splittings due to crystal structure have been calculated and measured for the first electronic transition and are of the order of 0.5 eV.[8,10] However, since our data average over directions we only observe the highly dominant member of the Davydov pair. Also, the molecular-orbital calculation gives peaks in the absorption coefficient, α, whereas we measure $\mathrm{Im}(1/\epsilon)$ with electron scattering. We have measured the energy-loss spectra from 0 to 100 eV at various values of momentum transfer and have performed a Kramers-Kronig calculation to obtain the dielectric response function and thus compare directly with α. Peak positions in the calculated absorption coefficient coincide with the energy-loss peaks to within about 0.2 eV (the accuracy of the molecular-orbital calculation) and only the lowest transition changes shape signficnatly, tending to peak sharply at the low-energy edge.

In this Letter we have demonstrated the power of inelastic electron scattering in investigating the role of symmetry in electronic transitions by the observation of monopole molecular-orbital transitions. Effects of other symmetry-breaking mechanisms such as crystal structure and impurities can now be systematically investigated. Our present results further support a previous experiment[9] in which the role of many-electron effects at soft x-ray absorption edges was tested using the same selection-rule change as was observed here.

We gratefully acknowledge discussions with C. B. Duke, A. J. Epstein, and D. J. Sandman.

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Diffusion of Hydrogen in Tantalum Studied by Motional Narrowing of Mössbauer Lines[*]

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(Received 14 August 1975)

The effects of H in Ta metal on the isomer shift and linewidth of the 6.2-keV Mössbauer resonance of ^{181}Ta have been studied as a function of H concentration and temperature. From the results, values for the activation energy of the H diffusion and for the mean residence time of the H atoms in Ta are derived.

The diffusional reduction of the linewidth (motional narrowing) is a well-established phenomenon in nuclear magnetic resonance and has been applied successfully in studies of diffusion.[1] Until now, similar motional-narrowing effects on Mössbauer resonance lines—though theoretically discussed[2] and observed in a limited case[3]—have not been utilized for obtaining quantitative information on the diffusion process. Using the high-resolution 6.2-keV γ resonance of ^{181}Ta,[4] we were able to observe the influence of the diffusion of H on the Mössbauer resonance in Ta metal. From the experimental results for the line shift and linewidth as functions of H concentration and temperature, the activation energy and the mean residence time of the diffusing H interstitial were derived. This opens a new microscopic method for studying the diffusion of H—and possibly other impurity atoms—in transition-metal hosts. The method is complementarily related to usual NMR studies of diffusion, since here the probes (the ^{181}Ta nuclei) are not diffusing by themselves, but are subjected to fluctuating interactions with the diffusing interstitials.

The experiments were performed on H-loaded Ta foils (4 mg/cm^2 thick; nominal purity 99.996 %), which were used as absorbers in Mössbauer transmission experiments with a single-line source of ^{181}W diffused into a single crystal of W metal. In order to ensure high purity, the Ta foils were degassed in ultrahigh vacuum ($\sim 10^{-9}$ Torr) and temperatures up to 2000°C. They were then electrolytically loaded with H in a $0.01N$ H_2SO_4 bath at current densities of about 100 mA/cm^2. The resulting H concentrations up to $c = 0.17$ (where c is defined as the H/Ta atom ratio) were obtained directly from the amount of H extracted at high temperatures from the loaded samples using a commercial vacuum-extraction apparatus.[5] According to the Ta-H phase diagram[6] and the experimental conditions, all samples studied were in the bcc α phase.

Some of the Mössbauer absorption spectra are presented in Fig. 1. The data were fitted with a single Lorentzian line modified by a constant dispersion term. This term describes the pronounced asymmetry of the lines and results solely from an interference between the Mössbauer ab-