Photoionization of Triphenylamine

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Summary A two-quantum photoejection process probably involving triplet excitation annihilation has been found in crystalline triphenylamine and its photoelectron spectrum has been measured.

We have found that upon irradiation of crystalline triphenylamine with light of energy less than the work function there is obtained a very weak photoelectric effect that does not follow the Einstein photoelectric law. The work function of crystalline triphenylamine in nitrogen is 5·53 eV as determined by the Millikan chamber technique previously described.[1–3] That the kinetic energy of the photoelectron is independent of light energy below threshold energy was shown by irradiating positively charged crystals suspended in the chamber with light of 3·9 eV until photoemission ceased in virtue of the positive charge induced; subsequent irradiation at 4·6 eV failed to produce a further photoelectric effect. Also the magnitude of the photoelectric current produced by light of less than the threshold energy was found to be proportional to the square of the light intensity.

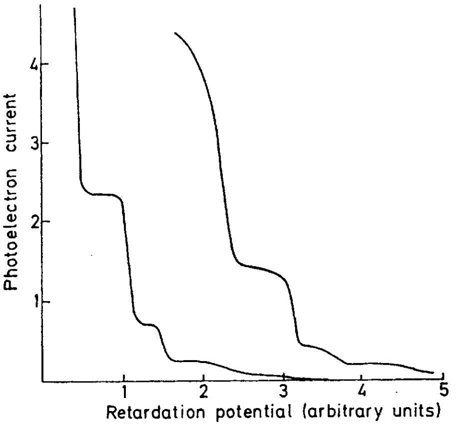

Figure 1. *Photoelectron retardation curves for photoemission of triphenylamine crystals by exciton annihilation. The two curves were obtained with two separate particles suspended in nitrogen at* −12 °C. *Light of energy* 4·13 eV *was obtained with a monochromator and a high-pressure mercury arc plus a thin glass filter.*

These observations are consistent with exciton annihilation as follows:

$$[Ph_3N]\ \text{crystal} + h\nu = [Ph_3N]^*\ \text{crystal} \qquad (1)$$

$$[Ph_3N]^*\ \text{crystal} \rightarrow [Ph_3N]\ \text{crystal} + \text{heat} \qquad (2)$$

$$[Ph_3N]^*\ \text{crystal} \rightarrow \text{exciton} \qquad (3)$$

$$2\ \text{exciton} \rightarrow \text{intermediate} \rightarrow [Ph_3N]\ \text{crystal} + [Ph_3N]^+\ \text{crystal} + e^-\ \text{gas} \qquad (4)$$

$$\text{exciton} \rightarrow [Ph_3N]\ \text{crystal} + \text{heat} \qquad (5)$$

Ph_3N^* is the initial excited state of triphenylamine and the 'intermediate' in reaction (4) is included to express the possibility of formation of a charge-transfer complex, excimer, *etc.*

The photocurrent is the rate of reaction (4) which is proportional to the square of the light intensity (as observed) if the rate of (5) greatly exceeds (4) but to the first power of the intensity if this inequality is reversed.

Using the Millikan chamber technique[3,4] it was possible to measure the maximum kinetic energy (5·86 eV) of the photoelectrons ejected by the double quantum process. Assuming that 5·86 eV is twice the energy of one exciton in reaction (4) and noting that the triplet energy in ethanol is *ca.* 3·1 eV[5] it appears that excitons are likely to involve molecules in their triplet states, the lowest singlet lying at *ca.* 3·6 eV.[5,6]

The retardation spectrum of crystalline triphenylamine was obtained by plotting the photocurrent against the positive charge on the particle as previously described.[7] Photoelectron spectra derived from retardation curves such as Figure 1 are given in Figure 2. Figure 2 (a) was obtained using low intensity light of 6·2 eV energy and 2 (b) was obtained with high intensity light of 4·13 eV. Thus in the (a) spectrum process (6) was involved and in the (b) spectrum process (4).

$$[Ph_3N]\ \text{crystal} + h\nu \rightarrow [Ph_3N]^+\ \text{crystal} + e^-\ \text{gas}. \qquad (6)$$

As previously described, the conversion of retardation potentials of the retardation curves into ionization energies of the photoelectron species requires the value of the work

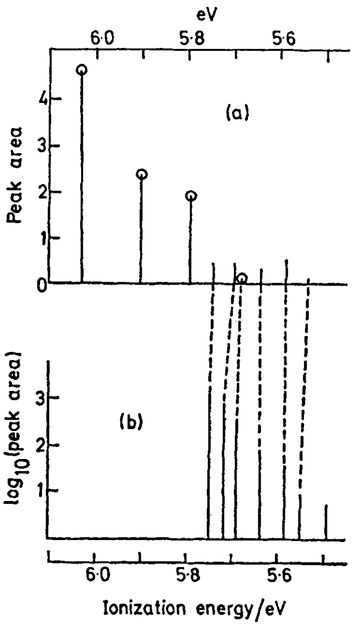

FIGURE 2. *Schematic photoelectron spectra of crystalline triphenylamine, the height of the lines representing the band areas of vibronic peaks and their positions being those of the peak maxima as derived from retardation curves. Curve* (a) *was obtained with light of* 6·2 eV *energy obtained with a monochromator and a deuterium arc plus a methanol filter; curve* (b) *was obtained with a monochromator and a high-pressure mercury arc plus a thin glass filter.*

function and it was assumed for this purpose that the appropriate work function for the (b) spectrum was the same as for the (a) spectrum. This would not be true if the products of the single and double quantum processes were different or if an intermediate of energy appreciably different from triphenylamine were involved in reaction (4); in either case spectra (a) and (b) would not be the same. However the average difference in energy between the six vibrational bands common to 2 (a) and 2 (b) is only 0·01 eV. It is arguable that a displacement by one or more vibrational progressions could lead fortuitously to such a result; however agreement in the interval of vibrational progression remains a test. There appears to be two such progressions in the (a) spectrum, one of 936 cm^{-1} [circled in Figure 2 (a)] and one of 429 cm^{-1}. Since the (b) spectrum cannot extend beyond 5·86 eV only one progression can be observed in it, the interval being 418 cm^{-1}, a value lying within experimental error of that in spectrum 2 (a). Thus as far as energy is concerned the spectra are the same and it is concluded that the only difference between the single and double quantum processes lies in the way in which the excitation energy is carried to the triphenylamine molecule.

Differences in the mode of excitation or in the energy of the exciting light would be expected to result in differences in the relative intensities of peaks in the photoelectron spectrum.[8] Accordingly the intensity distributions in 2 (a) and 2 (b) are not the same; specifically it is noted that the intensity of the 418 cm^{-1} progression in 2 (b) falls off approximately exponentially whilst in 2 (a) it diminished much more slowly.

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