AUTOIONIZATION IN ANTHRACENE CRYSTAL

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The fluorescence decay curves of Bergman, Levine, and Jortner are interpreted in terms of autoionization. It is shown that autoionization is always more important than collision ionization of excitons located on different sites.

In a recent Letter[1] Bergman, Levine, and Jortner have reported the fluorescence decay curves of the first excited singlet state of crystalline anthracene. The excitation was effected by a 100-MW short-pulse (20 nsec) Q-switched laser through a two-photon process. The interesting result of their experiment was that at the highest laser photon flux (1.8×10^{26} photons $\text{cm}^{-2}\,\text{sec}^{-1}$) available the authors obtained two decay curves, the one at earlier times ($t<50$ nsec) decaying twice as fast as the one at later times ($t>50$ nsec); the decay constants were found to be $k_1=10^8\ \text{sec}^{-1}$ and $k_2=5\times10^7\ \text{sec}^{-1}$, respectively. The authors have interpreted k_1 as being due to mutual annihilation of two excitons to give an electron-hole and unexcited molecule with a bimolecular rate constant $\gamma_S=3\times10^{-8}\ \text{cm}^3\,\text{sec}^{-1}$. The values for γ_S calculated by Choi and Rice[2] and by Sharma[3] are 2.5×10^{-12} and $3\times10^{-11}\ \text{cm}^3\,\text{sec}^{-1}$, respectively. Choi[4] and Sharma,[3] using the hopping model for excitons, have shown that the ionization probability falls as r^{-6} with distance, the nearest-neighbor interactions thus being the only important ones. Sharma[3] has shown, in addition, that in the multipole expansion of the interaction potential only the dipole-dipole term is important if the wave function representing the initial state of the ejected electron is taken to be the eighth Hückel molecular orbital and Slater functions are used to describe the $2p_z$ orbital of the carbon atom. The only previous experimental measurement of γ_S by Silver, Olness, Swicord, and Jarnagin[5] yielded a value of $5\times10^{-12}\ \text{cm}^3\,\text{sec}^{-1}$. Bergman, Levine, and Jortner explain the difference between the two measurements by the plausible assertion that the experiment of Silver et al. measures the rate of generation of free charge carriers which may be considerably smaller than the rate of ionization. Nevertheless, the interpretation of the experiment of Bergman, Levine, and Jortner, in terms of annihilation of two excitons to produce an electron-hole pair and a neutral atom, is still in conflict with the previous calculations. In this Letter we interpret the experiment of Bergman, Levine, and Jortner in terms of autoionization and show that autoionization is always a more important process than collisional ionization of excitons localized on two different sites.

If n is number of excitons per cc and N is number of sites per cc, the probability that the two excitons are localized in the same site is $\frac{1}{2}(n^2/N)$. The situation, however, is not static. If t is the time in seconds during which two excitons stay together, the number of excitons with which a given exciton shares the same site in 1 sec is n/Nt. If we further assume that during the time the two excitons share the same site they can undergo a unimolecular autoionizing decay with a rate constant $k\ \text{sec}^{-1}$, the probability that a given exciton has decayed after 1 sec is $(n/Nt)(1-e^{-kt})$ and the rate of decay, R_a, of excitons due to autoionization then is

$$R_a=\frac{1}{2}\frac{n^2}{Nt}(1-e^{-kt}). \tag{1}$$

Numerical values for k and t have now to be guessed. Manson[6] has calculated k for the $(2s)^2$ configuration of He to be $2.3\times10^{14}\ \text{sec}^{-1}$ and we will use this value for anthracene as well. It may be argued that the electron in the case of He has greater energy available and therefore has more accessible states which increase the rate constant. This factor, however, has to be considered together with the fact that a higher energy electron has a de Broglie wavelength of the order of atomic dimensions, and the rapidly varying phase of the electron tends to decrease the size of the transition matrix elements. The two effects oppose each other and it appears reasonable to take $k=2\times10^{14}\ \text{sec}^{-1}$. The value of t given by Nieman and Robinson[7] is 10^{-12}-$10^{-14}\ \text{sec}^{-1}$. On the other hand, the velocity of the singlet exciton is estimated from the corresponding Davydov splitting[1] to be 3×10^{-6} sec/cm. Assuming a mean distance of 8 Å between the sites, the average number of sites sampled by an exciton in its lifetime (20 nsec) is ~10^6. This gives us a value of $t = 10^{-14}$. Equation (1) then becomes

$$R_a = 1.24\times10^{-8}n^2, \tag{2}$$

where a value of 3.38×10^{21} has been subsituted for N. The bimolecular rate constant due to unimolecular autoionizing decay is in striking agreement with the γ_S postulated by Bergman, Levine, and Jortner to explain the results of their experiments.

If we assume the autoionizing mechanism to be the correct one, Eq. (2) tells us that autoionization of excitons will always be more important than the mutual annihilation of two excitons localized on two different sites, since the rate constant for the former process is three orders of magnitude larger than the rate constant for the latter process. Consequently, what has usually been assumed to be an exciton-exciton annihilation mechanism is really the autoionization of anthracene molecules, a process thus far not believed to occur.

This Letter actually poses more questions than answers. What is the nature of the excited state from which autoionization takes place? Can autoionization be observed by direct excitation of the anthracene crystal to the second excited singlet state, which overlaps the conduction-band edge believed to be at about 4.1 eV,[8] by suitable means? It is hoped that this Letter will motivate further experimental and theoretical studies to answer these and other questions.

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COULOMB DISPLACEMENT ENERGIES OF Ca-Sc ISOBARIC PAIRS*

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A new experimental technique was used to measure Coulomb displacement energies ΔE_c in the Ca-Sc isobaric pairs with $A = 44$, 46, 48, and 50. The reaction $Ca^{46}(He^3,d)Sc^{47}$ was used to measure this quantity for $A = 47$. This permits analysis of ΔE_c for all the isobaric pairs from $A = 41$ to 50, for the ground states and for several excited states, which yields a consistent picture.

The systematic accurate measurement of Coulomb energy differences ΔE_C between ground states (g.s.) and their isospin analogs has been the subject of a number of recent investigations.[1-3] A reaction for studying the analogs of 0^+ ground states is suggested by the property of the (t,p) reaction to strongly populate 0^+ states.[4] The (He^3,p) reaction, with a singlet deuteron transferred, is the isospin analog of the (t,p) reaction; we may therefore expect it to select the ground-state analogs, reduced in yield by the isospin vector-coupling coefficient which gives a factor of $(2T+2)^{-1}$. In fact, the $Ca^{40}(He^3,p)Sc^{42}$ (g.s.) transition[5] has been found to show the same characteristic $l = 0$ angular distribution as the (t,p) reaction.[4] We have studied the (He^3,p) reaction on the five even-A stable isotopes of Ca by use of the 12-MeV He^3 beam of the Argonne tandem Van de Graaff, with two angular settings of the broad-range magnetic spectrograph. Evaporated targets of ~50 $\mu g/cm^2$ of each isotope were used. In each case one strong proton group was found in the expected region of excitation; its energy shifted with the angle of observation in a way consistent with the target mass. To confirm our identification of the analog state in the case of Sc^{48}, we used the weak 15-MeV He^3 beam (obtainable with He^- injection) to expose a plate for the reaction $Ca^{48}(He^3,t)Sc^{48}$.[6] The value of ΔE_C was known for all the odd-A calcium isotopes except Ca^{47}, and that for the latter was obtained