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New aspects of the "channel three" problem in benzene, as revealed by multiphoton ionization photoelectron spectroscopy

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Combining a photoelectron spectroscopic technique with a $(1 + 1)$ resonant ionization method, we have investigated intramolecular decay processes of benzene in its S_1 state under collision-free conditions. Photoelectron spectra were obtained by selective excitation of benzene with a pulsed UV laser at several single vibronic levels of the S_1 state up to an internal energy (ΔE) of 5000 cm^{-1} . These spectra strongly suggest that the excitation of benzene at the vibronic bands above the onset of the "channel three" is followed by intramolecular vibrational redistribution within the S_1 state. It is concluded that there are no decay channels faster than this redistribution process up to $\Delta E = 5000\text{ cm}^{-1}$ at the first decay stage. The results of the integrated multiphoton ionization intensity distribution over the vibronic bands, as well as the internal-energy dependent spectral changes observed in the photoelectron spectra, also strongly suggest that the channel three is initiated by the redistributed vibrational modes, which lead to a fast internal conversion leads to the ground electronic state.

I. INTRODUCTION

One of the most puzzling problems in the field of radiationless transition is a sharp decrease in the fluorescence quantum yield in the S_1 state of benzene when the vibrational excess energy exceeds about $\Delta E = 3000\text{ cm}^{-1}$ (a "channel three" problem).¹ Very recently, Sumitani *et al.*² have presented quantitative aspects of channel three by using one-photon excitation of single vibronic levels (SVLs) up to $\Delta E = 5000\text{ cm}^{-1}$ (internal excess energy). So far, most of the arguments concerning the nonradiative pathway of benzene responsible for the channel three have traditionally been based on analysis of the fluorescence emission and the absorption line broadening.

Multiphoton ionization has been successfully employed for several years as a molecular spectroscopic tool.³ More recently, it has been demonstrated that a combination of photoelectron kinetic energy measurements and a multiphoton ionization technique provides a unique probe of excited-state dynamics in atoms and molecules.⁴ In our previous paper,⁵ we have also demonstrated for the first time the versatility of the multiphoton ionization photoelectron spectroscopy (MPI-PES) for studying ultrafast intramolecular relaxation processes of excited-state molecules under collision-free conditions.

In this paper, we present our MPI-PES results which clearly reveal rapid increases in the rate of intramolecular vibrational redistribution (IVR) above the onset of the channel three of benzene molecule. Combining the photoelectron spectral data with the integrated MPI intensity data obtained as a function of ΔE , we conclude that there are no faster decay channels other than the IVR above the channel-three region, and that the lifetime of the vibrationally redistributed S_1 state is longer than the order of 10^{-11} s in magnitude.

II. EXPERIMENTAL

The experimental setup of our MPI-PES method is schematically shown in Fig. 1. The present experiments were performed in a pulsed supersonic molecular beam to ensure isolated-molecule conditions. The sample was seeded by passing helium (1 atm) through a sample container at 20°C . Upon expanding into the first vacuum chamber the central portion of the gas jet is skimmed 10 mm downstream from the nozzle by a $\phi 2.0\text{ mm}$ skimmer. The gas expansion region is evacuated by a 5000 l s^{-1} oil diffusion pump. The molecular beam passes into the second chamber where interaction with the laser takes place at 40 mm downstream from the valve orifice. This chamber is pumped by a 1200 l s^{-1} diffusion pump with a water-cooled baffle and a liquid nitrogen cold trap. The beam passes through to the third chamber which is pumped by a 3000 l s^{-1} diffusion pump equipped with a liquid-nitrogen cold trap.

Measurements of photoelectron energy distributions were carried out with the MPI-PES apparatus already described elsewhere.⁴ Total ion currents were measured as a function of laser wavelength using a channeltron multiplier (Ceratron, Murata Co.). The output signal of the multiplier was amplified by a current amplifier (Keithley 427) and averaged by a boxcar integrator (N. F. Circuit Co.).

The laser wavelengths of 220–250 nm, used for excitation of benzene at several single vibronic S_1 levels, were covered by a Nd-YAG pumped dye laser combined with doubling and mixing crystals (Quanta-Ray, DCR-1, PDL-1, WEX). The laser beam was focused in the center of the second chamber with a lens of 50 mm focal length, where a molecular beam crosses the laser beam perpendicularly. The laser bandwidth used was $\sim 1\text{ cm}^{-1}$, and the laser intensity was monitored by a pin photodiode.

III. RESULTS

A series of the well separated SVLs denoted as $6^1 1^n$ ($n = 2, 3, 4$, and 5) were examined in the present work to

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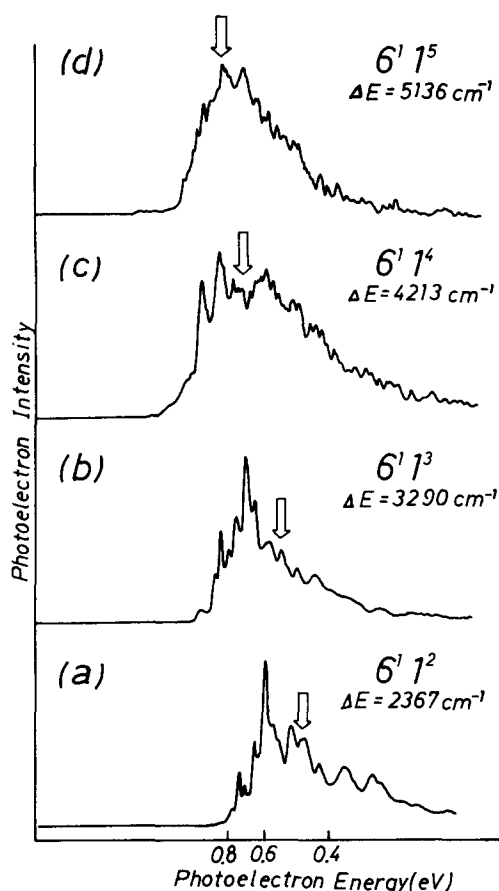


FIG. 4. The photoelectron spectra obtained by excitation of the SVLs of benzene; (a) $6'1^2$, (b) $6'1^3$, (c) $6'1^4$, and (d) $6'1^5$. The arrows indicate the positions of the expected $\Delta v = 0$ ionization transitions.

A similar spectral broadening with increasing internal excess energy has previously been observed in dispersed fluorescence spectra for many large molecules.¹³ Such broad fluorescence has been explained in terms of an IVR process which changes the nature of the emitting states. Actually, even in the case of benzene, O'Connor *et al.*¹⁴ have also very recently demonstrated that the excitation of benzene to its vibronic levels above 3000 cm^{-1} in the excess energy leads to structureless broad fluorescence which coexists with sharp SVL fluorescence bands.

In a resonant two-photon ionization process, if a very fast IVR takes place prior to the ionization transition, the resulting photoelectron spectrum would lose the memory associated with the optically prepared state. Then, the ionization transition would reflect the vibrational nature of the redistributed states. Such a situation has already been suggested in our previous paper,⁵ in which the broad features of photoelectron bands are presented for the ionization of benzene through vibrationally relaxed levels of its S_3 state ($^1E_{1u}$). In the present case, however, no electronic states other than the S_1 state can be responsible for the observed photoelectron spectra due to the energetic considerations. For example, the ionization of the isoenergetic triplet state should require at least an additional two photons to reach the ionic state which has the same internal excess energy as in the triplet state. Furthermore, if this $(1+2)$ ionization actually occurs, the resulting photoelectron bands should appear in the energy region which is about 3 eV above the

observed values. This is certainly not the case for the present experiments.

Let us now consider the ionization behavior of the vibrationally relaxed S_1 state of benzene. As is expected, the ionization transition from the S_1 state to the ground ionic state is electronically allowed by one-electron ionization. Thus, there is no restriction for the symmetry of vibrational quantum states of the ion that are formed. The vibrational structure of the photoelectron spectrum should only be governed by Franck-Condon overlaps between the S_1 and the ionic state. Furthermore, it should also be pointed out that the $\Delta v = 0$ ionization may be the most probable transition for the most of the redistributed vibrational modes, because the geometrical changes upon ionization are expected to be reasonably small for benzene molecule. Only a limited number of vibrational modes are considered to accompany a large displacement upon ionization. Thus, if we assume here that the IVR process populates many kinds of vibrational modes and quantum states, which are isoenergetic with the optically prepared state, then the superimposition of many $\Delta v = 0$ ionization transitions (involving partly the $\Delta v = \pm N$ transitions) will lead to the broadening of photoelectron spectrum, whose intensity peaks at $\Delta v = 0$. The expected spectral feature is schematically shown in Fig. 5. The intensity distribution peaking at $\Delta v = 0$ is apparent in the spectrum (d) of Fig. 4.

In contrast to the spectrum (d), the photoelectron spectrum (c) (shown in Fig. 4) consists of both sharp and broad bands. The two prominent sharp vibrational peaks are attributed to the $6'1^3_4$ ($I \leftarrow S_1$) and $6'1^2_4$ ($I \leftarrow S_1$) vibrations of the benzene cation. Since the ionization transition taking place from a real intermediate state should compete with other relaxation processes at this resonant intermediate state, it is easy to understand why the spectrum (c) consists of two types of photoelectron bands. According to a rate equation

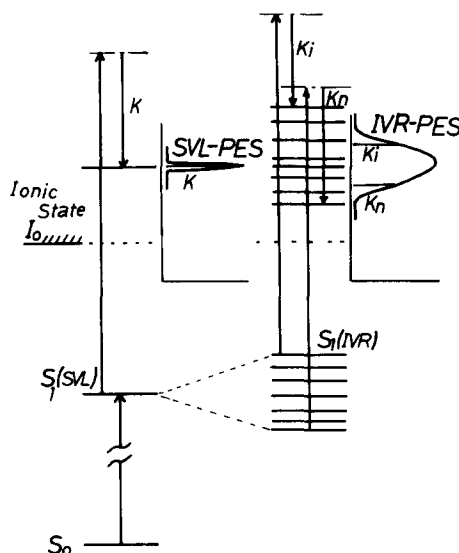


FIG. 5. A schematic drawing of the ionization band shapes expected for the photoelectron spectra through a vibrationally unrelaxed and relaxed levels, where only $\Delta v = 0$ ionization transitions are considered. The differences in photoelectron kinetic energies represented by K_i and K_n correspond to the differences in vibrational frequency changes upon ionization among many vibrational modes.

treatment for the present case, the intensity ratio of the sharp component to the broad one in each of the photoelectron spectra may simply be expressed by k_i/k_{ivr} , where k_i and k_{ivr} indicate the rate constants of the ionization and the IVR, respectively. Thus on the assumption that the k_{ivr} is much larger than the depopulation rate of the S_1 state (this assumption will be rationalized in the ensuing discussion) the spectral pattern seen in Fig. 4(c) can be understood by assuming that $k_i \approx k_{ivr}$.

Considering the laser power of $\sim 10 \mu\text{J}/\text{pulse}$ and the lens of 50 mm focal length, we may reasonably conclude that the ionization rate of the S_1 state of benzene is the order of magnitude of $10^{10-11} \text{ s}^{-1}$. This indicates that the IVR rate at the $6^1 1^4$ level ($S_1 \leftarrow S_0$) ($\Delta E = 4213 \text{ cm}^{-1}$) is also about the same order of magnitude. The lifetimes of SVLs above the channel three region have previously been discussed by Calmon *et al.*¹⁵ on the basis of their absorption linewidth measurements. According to their measurements, the decay rate for the $6^1 1^4$ level of the S_1 state of benzene has been determined to be $2.45 \times 10^{11} \text{ s}^{-1}$. Since the decay rate determined from the linewidth measurements should give an upper limit of the k_{ivr} for the corresponding SVL level, the observed decay rate may suggest that k_{ivr} is equal to or less than $2.45 \times 10^{11} \text{ s}^{-1}$ for the $6^1 1^4$ level. This value is in good agreement with the present value ($10^{10-11} \text{ s}^{-1}$) mentioned above. In order to discuss the rate constants more accurately, more quantitative experiments of laser power dependence are required. At the present time, however, even the rough rate-constant estimation mentioned above may have a merit for understanding the intramolecular decay processes. In this sense, it should be noteworthy to mention that the intensity of the sharp feature in the spectrum (c) weakens, while that of the broad band increases, and becomes dominant, as the laser power is decreased. Such a spectral change can be well understood by considering that the ionization rate is changeable with the laser power used.

We now discuss the channel three problem on the basis of the present results. At the first stage of the decay process, excitation of isolated benzene above the 3000 cm^{-1} excess energy is followed by a very fast IVR within the S_1 electronic state. This conclusion is supported by the following experimental results: (1) The intensity distribution of the $6^1 1^4_0$ ($S_1 \leftarrow S_0$) progression determined by the MPI method is almost the same as that of the absorption spectrum. This indicates that the ionization quantum yield is constant up to $\Delta E \approx 5000 \text{ cm}^{-1}$, independent of ΔE . (2) Even though the integrated MPI intensity is not affected by the amounts of excess energies, the IVR process apparently takes place, depending on the excess energy. As can be seen from the MPI photoelectron spectral changes in Fig. 4, the IVR rate increases significantly with the S_1 vibrational energy. At the vibronic state of $\Delta E \approx 5000 \text{ cm}^{-1}$, the IVR rate considerably exceeds the ionization rate of $k_i = 10^{10-11} \text{ s}^{-1}$. (3) From the viewpoints of both energetics and band shape, all of the new broad photoelectron bands can be understood by the ionization which occurs from the vibrationally redistributed S_1 state. In other words, there are no decay channels faster than the IVR process on the time scale shorter than the order of 10^{-11} s , and the IVR itself does not represent the population

decay of the S_1 state.

One of the most plausible second stages of the decay process is an internal conversion of the vibrationally redistributed S_1 state to the ground state. A possibility of enhancement of the intersystem crossing channel by IVR may be reasonably excluded by recent results of Otis *et al.*¹⁶ Recent theoretical treatments by Hornburger and Brand¹⁷ have shown that, with an assumption that the excess energy is democratically distributed among the vibrational states on a time scale shorter than the decay times for internal conversion or intersystem crossing, the relative internal conversion rate increases through the out-of-plane ν_4 vibration by about seven order of magnitude. Although it is not obvious at this time whether the IVR process populates all possible states with equal or unequal probability, it is quite likely that the resulting redistributed S_1 state at least partly involves the low-frequency modes such as the ν_4 and/or ν_{16} modes. A more microscopic inspection on the vibrationally relaxed state will be possible by using a higher resolution electron analyzer. The most important point here is that even the small population of the ν_4 mode may result in the anomalously large enhancement of the internal conversion rate, as suggested by Hornburger and Brand.¹⁷

Finally, it is possible to conclude that the channel three is caused by an enhancement of the internal conversion rate through the vibrational modes, which are optically inactive and formed only through a vibrational redistribution process above the onset. We have also demonstrated that the internal conversion rate at the relaxed state (k'_{ic}) is smaller than the order of 10^{11} s^{-1} . Furthermore, since the rate constants of both radiative¹⁸ and intersystem crossing to the triplet states¹⁶ are too small to account for the observed non-radiative decay rate,^{7,19} the observed fluorescence lifetime above the channel three must reflect the k'_{ic} value of the vibrationally redistributed S_1 state of benzene. In this sense, it should be pointed out that the lifetime varies from 0.9 to 0.02 ns with increasing internal excess energy.⁷ These k'_{ic} values are consistent with those evaluated from the present work. A similar mechanism for the nonradiative decay channel has also been suggested very recently by Otis *et al.*,¹⁶ but here we should again emphasize that the vibrationally redistributed S_1 state has a certain lifetime longer than 10^{-11} s even at the $\Delta E \approx 5000 \text{ cm}^{-1}$ level.

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