H atom elimination from the $\pi\sigma^*$ state in the photodissociation of phenol

Chien-Ming Tseng
Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan

Yuan T. Lee
Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan

Chi-Kung Ni (a)
Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan

(Received 3 June 2004; accepted 18 June 2004)

Photodissociation of phenol at 248 nm was studied using multimeter ion imaging techniques. Photofragment translational energy distribution of H atom elimination was measured. The results demonstrate that H atom elimination occurs on the $\pi\sigma^*$ excited state which has repulsive potential-energy functions with respect to the stretching of OH bond. It supports the recent ab initio calculation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1781153]

I. INTRODUCTION

Phenol–ammonia clusters have been studied extensively by fluorescence and multiphoton ionization spectra. From these studies, this system has long been considered as a model system to study excited state proton-transfer reactions in molecular clusters. (1–8) The excited state proton transfer results from the coupling of the covalent excited state PhOH(S$_1$)–(NH$_3$)$_n$ with ionic excited-state PhO$^-\sigma^*$–(NH$_3$)$_n^+$ (NH$_3$)$_{n-1}$.

Recently, Jacoby and co-workers have shown that the REMPI spectra of PhOH–(NH$_3$)$_3$ and PhOH(NH$_3$)$_4$ show well resolved vibronic structure when the (NH$_3$)$_n^+$ mass peaks are monitored, while excitation spectra of PhOH–(NH$_3$)$_n^+$ mass peaks are structureless. (9) Pino et al. have reported that the (NH$_3$)$_n^+$ mass peaks can be observed even if the ionization laser is delay for 200 ns from the ultraviolet laser for excitation to the S$_1$ state. (10,11) The result indicates the product, (NH$_3$)$_3^+$H$^+$, is generated from the ionization of a long lived neutral species. Instead of the excited state proton transfer, these experimental data were interpreted as the H atom transfer in the S$_1$ state. This hydrogen transfer mechanism is also supported by the infrared dip spectroscopy (12) and time-resolved infrared spectra (13) of the photochemical reaction products of phenol–ammonia clusters.

Ab initio calculations have been performed for the electronic ground and lowest excited singlet states of phenol and the complexes of phenol with ammonia. (14–16) An excited singlet state of $\pi\sigma^*$ character, which has repulsive potential-energy functions with respect to the stretching of OH bond was found. The $\pi\sigma^*$ potential energy functions intersect the low lying $\pi\sigma^*$ state.

II. EXPERIMENT

The experimental techniques have been described in detail in our previous reports, (17–19) and only a brief description is given here. Molecules in the molecular beam were photodissociated by a UV laser pulse at 248 nm. Due to the recoil velocity and center-of-mass velocity, the fragments were expanded to a larger sphere on their flight to the ionization region, and then ionized by a VUV laser pulse at 118 nm. The distance and time delay between VUV and UV laser pulses were set such that VUV laser passed through the center-of-mass of dissociation products and generated a line of ionized products. The length of the line was proportional to the fragment recoil velocity in the center-of-mass frame multiplied by the delay time between the photolysis and the ionization laser pulses. To separate the different masses within the ion segment, a pulsed electric field was used to extract the ions into a mass spectrometer after ionization. While the mass analysis was being executed in the mass spectrometer, the length of each fragment ion segment continued to expand in the original direction according to its recoil velocity. At the exit port of the mass spectrometer, a two-dimensional ion detector was used to detect the ion positions and intensity distribution. In this two-dimensional detector, one direction was the recoil velocity axis and the other...
was the mass axis. The identification of the dissociation products and the measurement of their translational energy distributions were therefore simultaneously obtained from the image.

III. RESULTS AND DISCUSSION

Fragment ion of $m/e = 93$ ($C_6H_5O^+$) with large intensity was observed from the photodissociation of phenol at 248 nm. It corresponds to the H atom elimination. The images of $m/e = 93$ obtained at various delay times between pump and probe laser pulses are shown in Figs. 1(a) and 1(b). As the delay time between pump and probe laser pulses increased, the length of the $m/e = 93$ image increased rapidly. This corresponds to the $C_6H_5O$ fragment with large recoil velocity. The photofragment translational energy distribution obtained from the image is shown in Fig. 2. It shows that the average released translational energy is large, and the peak of the distribution is located at 15 kcal/mol. It is interesting to note that the maximum translational energy reaches the maximum available energy of the reaction $C_6H_5OH + h\nu$ (248 nm) $\rightarrow C_6H_4O + H$. In addition to $m/e = 93$, fragment ions of $m/e = 76$, 66, and 65 with small intensities were also observed. However, these signals are very small and they are not related to the H atom elimination. They will not be discussed in this work.

UV absorption of phenol at 248 nm corresponds to the excitation of the $S_1$ state. Since $S_1$ is a stable state, dissociation must occur through the coupling of this bound state with a repulsive state, or after the internal conversion or intersystem crossing to a lower electronic state. $\pi\sigma^*$ is a repulsive state and $S_0$, $T_1$, and $T_2$ are the electronic states which have energies lower than that of $S_1$. Dissociation must occur on one of these states. The large translational energy release in the H atom elimination channel indicates that the dissociation must occur from an excited state of repulsive potential, or from an electronic state with a large exit barrier. This eliminates the dissociation probability on the $S_0$ state. The potential energy surface of the triplet state that correlates to the dissociation products of two radicals in the ground state may have an exit barrier and the released translational energy can be large. Therefore, it is possible that the large translational energy release results from the triplet state dissociation after intersystem crossing. However, photodissociation of phenol at 193 and 253 nm in the condensed phase studied by Fourier transform electron paramagnetic resonance and transient absorption spectroscopy shows that triplet state is not involved in the dissociation process.

Recent ab initio calculation shows that the $\pi\pi^*$ state, which has repulsive potential-energy functions with respect to the stretching of OH bond, intersects not only the bound potential energy functions of the $S_1(\pi\pi^*)$ excited state, but also that of the electronic ground state. The minimum of the $S_1(\pi\pi^*)$ state is located at 4.5 eV above $S_0$, and the $\pi\pi^* - \pi\sigma^*$ conical intersection is at ~5 eV. The internal conversion from $S_1$ to $S_0$ and intersystem crossing from $S_1$ to $T_1$ are the dominant decay channels for the phenol molecules after the excitation by 4.5 eV photons. However, as the excitation photon energy increases to 5 eV, the $\pi\pi^* - \pi\sigma^*$ conical intersection must greatly enhance the predissociation of the optical excited $\pi\pi^*$ state by the optically dark $\pi\sigma^*$ state, resulting in the H atom elimination on the repulsive $\pi\sigma^*$ state. The conical intersection between $\pi\sigma^*$ and $S_0$ provides the other population transfer from $\pi\sigma^*$ to $S_0$ and the dissociation products are produced in the electronic ground state. The observation of large translational energy release in our experimental measurement indicates that H atom elimination must be a dissociation process on the repulsive $\pi\sigma^*$ surface. It provides a direct evidence of the $\pi\pi^* - \pi\sigma^*$ predissociation mechanism of phenol at 248 nm.

ACKNOWLEDGMENTS

The work was supported by the National Science Council Taiwan, under Contract No. NSC 92-2113-M-001-015.