

ZEKE-PFI spectroscopy of naphthalene vapours via S_2 electronic state

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ABSTRACT

A new group of electrons in the naphthalene ZEKE PFI spectrum has been observed in the energy range 70000 - 72000 cm^{-1} by the one-color two-step laser excitation technique. It can be assigned to the field ionization of the high n Rydberg states converging to the first electron-excited ionic state of naphthalene. The lifetimes of the superexcited Rydberg states with the energy excess (above the first ionization energy) up to 1 eV are about 1 μs . The improved value of the second adiabatic ionization potential is $71823 \pm 30 \text{ cm}^{-1}$ ($8.904 \pm 0.004 \text{ eV}$).

Keywords: photoionization methods, ZEKE-PFI spectroscopy, naphthalene.

INTRODUCTION

In this work we have performed the zero-kinetic-energy pulsed-field ionization (ZEKE PFI) studies of naphthalene vapors with the help of a new laser spectrometer. The method of ZEKE-PFI photoelectron spectroscopy has become a widely used tool for investigation of the molecular ion energy spectra. Naphthalene, as a prototype aromatic molecule with a conjugated π -system is a traditional object of spectroscopic studies¹⁻⁸. Energy spectra of neutral molecule of naphthalene and its cation were successfully investigated by absorption and luminescence spectroscopy and by laser photoionization spectroscopy as well⁹⁻¹⁴. So we have chosen the naphthalene to test our spectrometer. The obtained ZEKE-PFI spectrum has revealed a new group of electrons. We assign it to the field ionization of the high n Rydberg states converging to the first electron-excited state of cation. These states are populated resonantly via S_2 electron state of naphthalene. The new group enabled us to improve the value of the second adiabatic ionization potential - $71823 \pm 30 \text{ cm}^{-1}$ ($8.904 \pm 0.004 \text{ eV}$).

EXPERIMENT

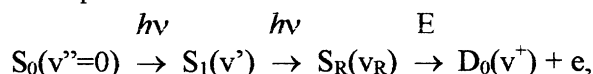
The experimental setup for ZEKE-PFI spectroscopy is based on a new laser spectrometer. This spectrometer enables one to carry out the following methods of photoionization spectroscopy: total current spectroscopy; mass-spectroscopy; photoelectron spectroscopy; ZEKE- and ZEKE-PFI spectroscopy. A tunable dye laser, pumped by the 2-nd harmonic of Nd-YAG, is used to populate the high n Rydberg states. The beam of the frequency-doubled radiation is focused into the ionization chamber by the short-focus lens ($F=140 \text{ mm}$). The ionization chamber is filled with naphthalene vapors at the pressure of about 10^{-5} Torr and at room temperature. The laser wavelengths were calibrated by Hg lamp with the accuracy of 0.05 nm. Wavelengths were scanned with the 0.02 nm step. The laser pulse duration is 12 ns, the energy in pulse is 1-15 μJ .

Photoelectrons are removed from the viewing field of detector by the dc field of $\sim 0.1 \text{ V/cm}$. The Rydberg states with $n > 130$ are ionized by the delayed (0-1 μs) electric

field pulse (~ 1 V/cm). Thus formed electrons (ZEKE PFI electrons) are detected by chevron pair of microchannel plates (MCP).

RESULTS

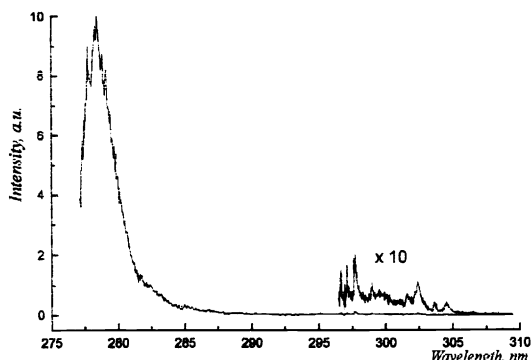
The one-color two-step ZEKE-PFI spectrum is shown in Fig.1. It consists of the two groups of electrons - nearly 300 nm and nearly 279 nm, respectively. The first one corresponds to the two-step excitation of the Rydberg states converging to ground ionic state of naphthalene D_0 . This group (Fig.2) has been studied thoroughly in other laboratories (see the two-color excitation of jet cooled naphthalene¹³). It is assigned to the following sequence of processes:



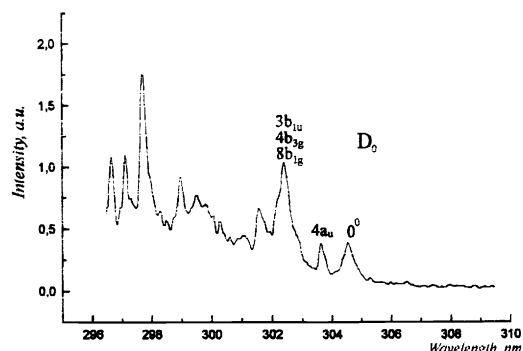
where S_0 is a ground electron state; S_1 - first excited state; S_R - Rydberg states converging to the different vibrational terms of the ground D_0 state of cation; v'' , v' , v_R and v^+ - series of vibrational quantum numbers; E - ionizing electric field.

Thus formed electrons have almost zero kinetic energy, because the ionized Rydberg states lie 4-6 cm below the threshold (at field intensity ~ 1 V/cm).

Analysis of ZEKE-PFI spectra via S_1 state made it possible to identify the vibrations of D_0 state of cation^{13,14}. We used this information to analyze the structure of the first group of electrons.



ZEKE-PFI spectrum of naphthalene
(Fig.1)



"Known" group
(Fig.2)

The structure can depend both on the one-photon absorption spectrum structure in the region of $S_0 \rightarrow S_1$ transition and on the satisfying the conditions of the double optical resonance:

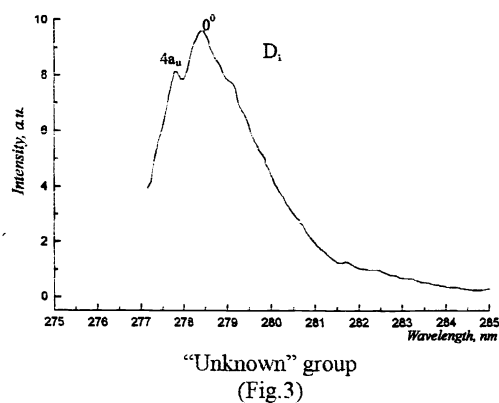
$$2\nu \approx I_i + E_\nu(M^+) - E_{\nu''}(M) \quad (1)$$

where ν is the wave number, I_i - i -th adiabatic ionization energy, $E_\nu(M^+)$ and $E_{\nu''}(M)$ - vibrational energies of the ionic and initial electron states, correspondingly. Energy is measured in cm^{-1} . The equation (1) isn't exact due to neglecting the rotational excitation of molecules and ions, laser radiation bandwidth and dispersion of "zero" electron energies ($4\text{-}6 \text{ cm}^{-1}$).

Spectrum of naphthalene vapors luminescence excitation was obtained³ at the conditions, similar to ours. Its comparison with the one-color ZEKE-PFI spectrum reveals no correlation. Therefore, we assign the obtained structure to the set of electron-vibrational states of cation. The long-wave peak ($65674 \pm 20 \text{ cm}^{-1}$) corresponds to the first adiabatic ionization potential of naphthalene ($65687 \pm 7 \text{ cm}^{-1}$)¹³. The next peak is at $200 \pm 30 \text{ cm}^{-1}$ distance. We assign it to the excitation of $4a_u$ vibration of cation (176 cm^{-1})¹⁴. Wide peak with maximum at 302.5 nm is at $450 \pm 30 \text{ cm}^{-1}$ distance from 0^0 peak. This peak is complex. Its high intensity is defined by the superposition of the following vibrations: $3b_{1u}$ (423 cm^{-1}), $4b_{3g}$ (425 cm^{-1}) and $8b_{1g}$ (455 cm^{-1}). The long-wave shoulder can correspond to $3b_{2g}$ (365 cm^{-1}) and/or $8b_{2u}$ (365 cm^{-1}) vibrations. Short-wave increase of the intensity of electron background is provided by the noticeable role of hot transitions and by the short-wave increase of the vibrational states density of cation. Hot transitions are responsible for red shadowing of all peaks, because most of the low-frequency ion vibration energies are less than that of the initial, S_0 state^{6,14}.

One can see that it is possible to obtain the useful information from one-color experiments, which are far easier to carry out.

The second group of ZEKE-PFI electrons (near 279 nm) has been observed for the first time. This group is depicted in Fig.3. We can assign it to the pulsed-field ionization of the Rydberg states converging to the first electron-excited state of cation D_1 . The second adiabatic ionization energy was determined by photoelectron spectroscopy. The value of this energy varies within 8.7-9.0 eV limits¹⁵⁻¹⁷. The two-step ionization ($S_0 \rightarrow \dots \rightarrow D_1$)



becomes possible at the wavelengths less than $\sim 285 \text{ nm}$. Both S_1 and S_2 electron-vibrational levels can serve as an intermediate one in this process. The most accurate value of the difference between $S_2(0^0)$ and $S_0(0^0)$ terms is $35815 \pm 5 \text{ cm}^{-1}$ (4.44 eV), derived from the dependence of radiative lifetimes of electron-vibrational states of naphthalene upon excitation energy⁵. This value is approximately in the center of the gap between $D_1(0^0)$ and $S_0(0^0)$. The one-color two-step excitation is possible due to this intermediate level. Two-photon energy on the short-wavelength limit of laser radiation band exceeds the second ionization threshold by $\sim 200 \text{ cm}^{-1}$. Accordingly, the second group is formed involving ground (or low) vibrational levels of S_2 state. When the equilibrium geometries of S_2 , S_R and D_1 states are similar, the Frank-Condon factors of the transitions are high¹⁴. In fact, in energy region higher, than $S_2(0^0)$, molecular states of naphthalene are mixed due to electron-vibrational interaction of S_1 and S_2 states^{2,3,8}. The oscillator force of $S_0 \rightarrow S_2$ transition is 50 times greater than that of $S_0 \rightarrow S_1$ transition^{8,18}; Frank-Condon factors for latter transitions with energies higher than 3800 cm^{-1} are very small. This leads to the optical coupling of S_0 and S_2 components of molecular state. The intensity ratio of two our groups is defined by the oscillators' forces ratio.

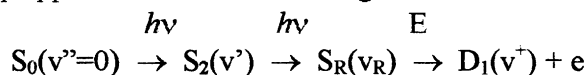
The results of semi-empirical calculations tell us that the equilibrium geometries of S_1 , D_0 and D_1 are similar (average deviation is 0.8%, maximal deviation - 2.7%)¹⁴. In this case the transitions with big changes of vibrational energy will be characterized by small Frank-Condon factors and the preference will be given to transitions with the conservation of vibrational energy ($\Delta v_i = 0$)¹⁹. The fact, that in most of multi-photon (photoelectron) spectra transitions with small Δv_i have maximal intensity¹², just adds to our arguments.

Molecular states of naphthalene, lying above the $S_2(0^0)$ level, can have admixture of low-lying triplet states^{3,4}. However, the same, as for S_1 state, reasons, lead us to the thought, that these states add a little to our signal.

The short-wave group is almost structureless, though there are two distinct peaks at the distance $174 \pm 20 \text{ cm}^{-1}$. It corresponds (concerning the uncertainty in determining the wavelengths) to the $4a_u$ vibration of D_0 state of naphthalene cation¹⁴. This vibration is seen in the first group. There are no data for out-of-plane vibrations in D_1 , but whereas potential surfaces of D_0 and D_1 states are quite close, we assign the main peak to the generation of cation in ground state $D_1(0^0)$ and the second one - in $D_1(4a_u)$ state. In this case the second adiabatic ionization potential value is $71823 \pm 30 \text{ cm}^{-1}$ ($8.904 \pm 0.004 \text{ eV}$). This value improves the less accurate values, obtained by photoelectron spectroscopy¹⁵⁻¹⁷.

CONCLUSION

The new laser spectrometer was successfully tested on a naphthalene vapors. We have observed a new group of electrons near 279 nm in one-color two-step ZEKE-PFI spectrum. This group appears due to the following chain of elementary processes:



The superexcited Rydberg states converging to D_1 have long lifetimes. (The decay of these states via all decay channels including autoionization is characterized by $\sim 1.0 \mu\text{s}$ period).

We assume that one of the two distinct peaks in a new group corresponds to the second adiabatic ionization potential, the improved value of which is $71823 \pm 30 \text{ cm}^{-1}$ ($8.904 \pm 0.004 \text{ eV}$) and the second one - to the generation of cation in $D_1(4a_u)$ state, correspondingly (the energy of $4a_u$ vibration is $174 \pm 20 \text{ cm}^{-1}$).

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