MOLECULAR
SPECTROSCOPY

One-Color Spectroscopy of Threshold Electrons Produced in Pulsed Ionization of High-Lying Rydberg States of Naphthalene by an Electric Field

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Abstract—In a one-color spectrum of threshold electrons produced in pulsed ionization of long-lived (0.1–1.0 μs) Rydberg states of naphthalene by an electric field, a new group of electrons was observed. It was attributed to the two-step excitation of high-lying Rydberg states of a molecule, which converge to the first excited electronic state of a cation. A refined value of the second adiabatic ionization energy of naphthalene was obtained (8.913 ± 0.004 eV).

INTRODUCTION

Naphthalene is a classical object of spectroscopic studies as one of the simplest molecules with a conjugate system of π electrons whose symmetry is lower than the benzene symmetry (see [1–8] and references therein). Spectra of energy states of a neutral molecule and a cation of naphthalene and the vibronic interaction in these molecular systems were studied with advantage not only by the traditional methods of absorption spectroscopy and luminescence, but by the methods of laser photoionization spectroscopy as well [9–14]. The presence of spectroscopic information and the optical range convenient for work formed the basis for the choice of the naphthalene molecule as a test molecule for the adjustment of operating modes of the laser photoionization spectrometer made by us. In the spectrum of threshold electrons produced by pulsed electric-field ionization of Rydberg states with large values of the principal quantum number [ZEKE PFI (zero-kinetic energy electrons produced by pulsed field ionization) spectrum], a new group of electrons was found. It was attributed to the ionization of long-lived (with lifetime ~ 0.5 μs) Rydberg states converging to the first excited electronic state of a naphthalene cation. The Rydberg states were populated by one-color two-step excitation via the S_2 electronic state of a molecule.

EXPERIMENTAL

The measurements were made with the aid of a laser spectrometer enabling one to realize the following methods of photoionization spectroscopy: total-current spectroscopy, mass spectrometry, photoelectron spectroscopy with a fixed laser radiation energy, and threshold photoelectron spectroscopy (ZEKE PFI spectroscopy). To excite Rydberg states, we used a tunable LZhI-506 dye laser, which was pumped by the second harmonic of an LTI-PCh Nd:YAG laser. The frequency

of radiation of the dye laser (we used rhodamine 6G and rhodamine C dyes) was doubled in a KDP crystal, and the beam outgoing from it was focused by a lens with focal distance of 14 cm into an ionization chamber through which naphthalene vapors with pressure of the order of 10^{-3} Pa were pumped. The wavelength scale was calibrated with an accuracy of 0.05 nm with the aid of a PRK-4 mercury lamp. The minimum scan step was 0.01 nm. Laser pulses had duration of 12 ns and energy in a range of 1–15 μJ.

To obtain ZEKE PFI spectra with a variable delay time (in a range of 0–1 μs) with respect to a laser pulse, one forms in the excitation region the electric field ~1 V/cm, which ionizes Rydberg states with $n > 130$. Charged particles produced during the action of a laser pulse are removed from the excitation region by the 0.1-V/cm field before a pulse of the ionizing electric field is applied to the system. The electrons produced by ionization of Rydberg states are pulled out, accelerated, and detected by a chevron pair of microchannel plates.

RESULTS AND DISCUSSION

Figure 1 presents a survey one-color ZEKE PFI spectrum of naphthalene vapors, which consists of two groups of electrons in regions of 305–296 and 281–278 nm. The long-wavelength group was observed earlier in [13], with the aid of a two-color excitation of naphthalene molecules in a supersonic beam and was assigned to the following sequence of elementary processes:

$$S_0(v'' = 0) \xrightarrow{h\nu} S_1(v') \xrightarrow{h\nu} S_R(v_R) \xrightarrow{E} D_0(v^+) + e,$$
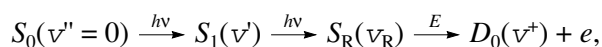
where S_0 and S_1 are the ground and first excited singlet states of a molecule, S_R are Rydberg states converging to different vibrational terms of the ground doublet states of the cation D_0, v'', v', v_R, and v^+ are sets of vibrational quantum numbers, and E is the electric field
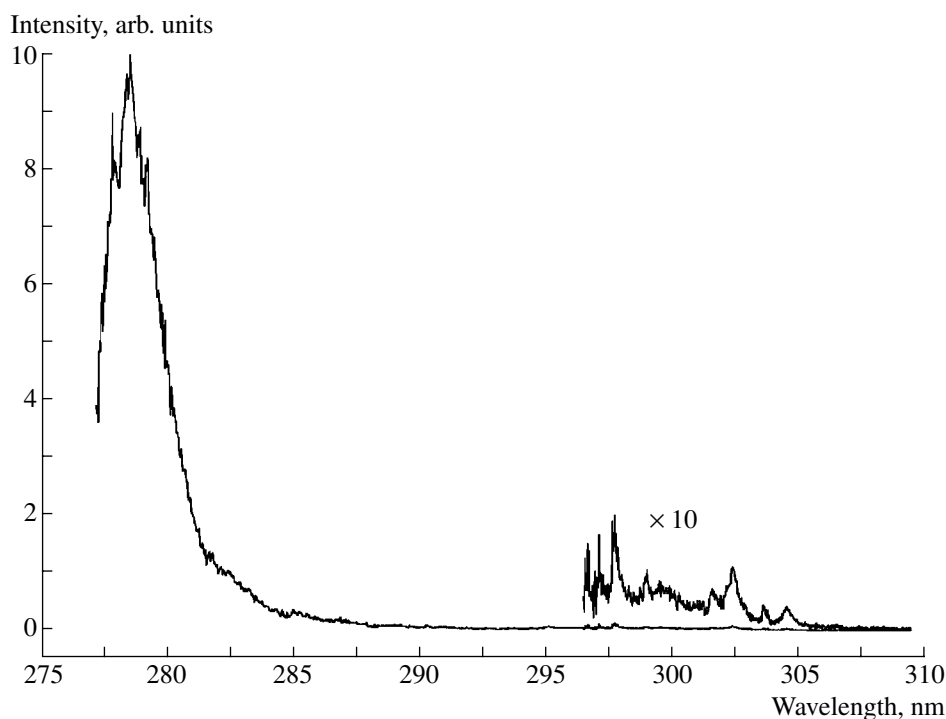
Intensity, arb. units

Fig. 1. Survey ZEKE PFI spectrum of naphthalene.

ionizing Rydberg molecules. The kinetic energy of electrons produced in the system is close to zero because the Rydberg states being ionized lie in a narrow energy band (4–6 cm^{-1} wide for a field strength of 1 V/cm) near the threshold of production of a cation in the corresponding quantum state.

The structure of the long-wavelength group of the ZEKE PFI spectrum (Fig. 2) can be caused both by the resonances of one-photon absorption in the region of the $S_0 \longrightarrow S_1$ transition and by the condition of the dou-

Intensity, arb. units

Fig. 2. The spectrum in a region of 296–310 nm on an expanded scale.

ble optical resonance for the generation of electrons with a near-zero kinetic energy (threshold electrons):

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

Here, $h\nu$ is the energy of laser quanta, I_i is the adiabatic energy of ionization accompanied by the formation of an ion in the ith electronic state, and $E_\nu(M^+)$ and $E_{\nu''}(M)$ are the energies of vibrational excitation in the final (ionic) and initial states. The equality is approximate because we did not take into account the rotational excitation of molecules and ions, a small (4–6 cm^{-1}, see above) energy spread of the Rydberg states being ionized, and the nonmonochromaticity of radiation.

In [3], the excitation spectrum of $S_1 \longrightarrow S_0$ luminescence of naphthalene vapors is presented, which was obtained under conditions that are the most close to our experiments. The comparison of this spectrum with the one-color ZEKE PFI spectrum gives evidence of the absence of correlation between their structures. Because of this, we attribute the structure observed in the ZEKE PFI spectrum to the structure of vibronic terms of a cation. The most long-wavelength peak at 304.5 nm corresponds to a threshold energy of $65\,674 \pm 20$ cm^{-1}, which agrees within the limits of experimental error with the adiabatic ionization energy of naphthalene ($65\,687 \pm 7$ cm^{-1} [13]), which is known with a high accuracy. Because of this, we attributed it to the production of naphthalene ions in the unexcited vibrational states. The next peak is offset from the 0° peak by 200 ± 20 cm^{-1} on the scale of doubled frequencies of laser
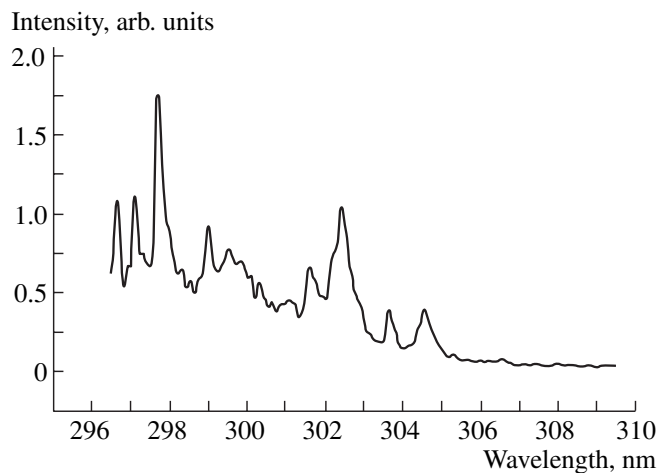
radiation, and it was attributed to the excitation of one quantum of the $4a_u$ mode of a cation with a frequency of 176 cm^{-1} [14]. The intense wide peak with a maximum at 302.4 nm, which is offset by 468 ± 20 cm^{-1} with respect to the 0° peak, is complex and may correspond to the excitation of vibrations of the $3b_{1u}$(423 cm^{-1}), $4b_{3g}$(425 cm^{-1}), and $8b_{1g}$(455 cm^{-1}) type, whereas the long-wavelength shoulder of this peak may be associated with excitation of the $3b_{2g}$(365 cm^{-1}) and/or $8b_{2u}$(365 cm^{-1}) modes. The overlap of several transitions results in an increased intensity of the peak at 302.5 nm.

As the wavelength of exciting radiation is decreased, the structure of the spectrum becomes smoothed and the intensity of the continuous electron "background" increases. This is caused by an increase of the density of vibrational states of a cation and a noticeable role of hot transitions under conditions of our experiments (the vapor pressure was 300 K). Note that the red shading of bands is associated with hot transitions as well, because the frequencies of the majority of low-frequency vibrations of an ion are lower than the corresponding frequencies of the S_0 state of naphthalene [6, 14]. In our opinion, there was little sense in carrying out the analysis of the spectrum in the region up to 290 nm in more detail because the ZEKE PFI spectra in this region under conditions of two-color excitation of naphthalene in a supersonic beam, which contain more information, have been already published and analyzed [13, 14]. However, note that our data give evidence of the feasibility of obtaining valuable data on the spectrum of energy states of ions with the aid of a one-color version of ZEKE PFI spectroscopy, which is easy to realize.

The main result of our work is associated with the observation of a new group of ZEKE PFI electrons in a short-wavelength region (Fig. 3), which was attributed to the electric-field ionization of Rydberg states converging to the first excited electronic state of the cation D_1. The adiabatic energy of naphthalene ionization with D_1 production was determined only by the method of He I photoelectron spectroscopy and lies in a range of 8.7–9.0 eV [15–17]. In the case of two-step excitation, the production of naphthalene ions in this state from the unexcited S_0 state of the molecule is possible in the spectral region below ~285 nm, which corresponds to the region of observation of the new signal. Intermediate states may represent vibronic levels of both S_1 and S_2 states. The most reliable value of the energy of the 0° term of S_2 with respect to S_0(0°) is $35\,815 \pm 5$ cm^{-1} (4.44 eV), which was determined from the dependence of the radiative lifetime of vibronic states of naphthalene on the wavelength of exciting radiation [5]. This value lies at the middle of the spacing between the S_0(0°) state of a molecule and the D_1(0°) state of a cation, which provides the possibility of excitation of Rydberg states converging to D_1(0°) in one-color experiments (1). At the short-wavelength
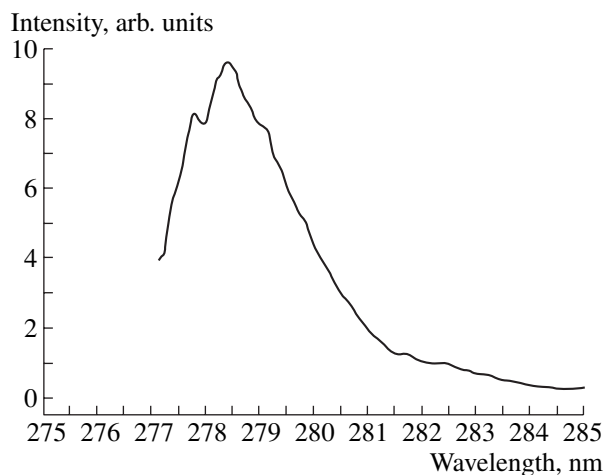

Fig. 3. The spectrum in a region of 285–278 nm on an expanded scale.

limit of our measurements ($\lambda \approx 278$ nm), the energy of two photons exceeds the threshold energy of the D_1(0°) formation by approximately 200 cm^{-1}. Thus, with no regard for hot transitions, the second group of electrons is produced with participation of unexcited (weakly excited) vibrational levels of the S_2 state. In view of the close values of equilibrium geometrical parameters of the S_2, S_R, and D_1 states [14], such transitions are characterized by large values of Franck–Condon factors.

In reality, the molecular states of naphthalene in the region above the energy of the S_2(0°) state are mixed owing to the vibrational interaction of the S_1 and S_2 states [2, 3, 8]. However, in view of the fact that the oscillator strength of the $S_0 \longrightarrow S_2$ transition exceeds the oscillator strength of the $S_0 \longrightarrow S_1$ transition by at least a factor of 50 [8, 18] and the Franck–Condon factors for the excitation of vibrational levels of S_1 with excitation energy greater than 3800 cm^{-1} [the energy spacing between the S_1(0°) and S_2(0°) states] are small, the S_2 component of the molecular state is optically coupled with S_0. A large oscillator strength of the $S_0 \longrightarrow S_2$ transition accounts also for a considerably higher intensity of the short-wavelength group of electrons in the ZEKE PFI spectrum (Fig. 1).

The S_1 component of the intermediate state is bound to give only a little contribution to the ZEKE PFI spectrum in the region of 285–278 nm. Indeed, the vibrational excitation energies of the isoenergy S_1 and S_2 levels differ by ~3800 cm^{-1}. According to the semiempirical quantum-chemical calculations, the geometrical characteristic of equilibrium configurations of the S_1, D_0, and D_1 states differ only little (the average distinction is about 0.8% and the maximum one is 2.7%) [14]. According to the Franck–Condon principle, for small distinctions of equilibrium geometrical parameters of the states being combined, the transitions with conservation of vibrational energy have the highest probability

(the $\Delta v_i = 0$ rule [19]). The production of naphthalene ions in the D_1 state with this energy of vibrational excitation needs radiation with $\lambda < 265$ nm. As for the production of threshold electrons owing to the $S_1 \longrightarrow D_0$ transition, it is bound to be accompanied by the change of vibrational energy from 3800 to ≥ 6500 cm^{-1} (the difference of the first two ionization energies of naphthalene), These transitions have a low probability. Indeed, in the majority of photoelectron spectra, the intermediate S_1 states manifest themselves with the highest probability in the transitions with conservation or a small change of vibrational energy [12].

The molecular states of naphthalene in the region above the 0° level of S_2 may also have an admixture of low-lying triplet states [3, 4]. However, in view of the reasoning used above for the S_1 component, their contribution to the signal observed in the experiment must be small.

Thus, the short-wavelength group of ZEKE PFI electrons is produced mainly by the following sequence of elementary processes:

$$S_0(v'' = 0) \xrightarrow{h\nu} S_2(v') \xrightarrow{h\nu} S_R(v_R) \xrightarrow{E} D_1(v^+) + e.$$
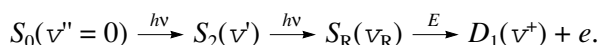
Note that the Rydberg states converging to D_1 are overexcited, with an energy excess of 0.8–1.0 eV above the first adiabatic ionization energy. In spite of this fact, they are long-lived and have large lifetimes (0.1–1.0 µs) with respect to all decay channels, including autoionization.

The short-wavelength group of ZEKE PFI electrons has almost no structure. In this group, only two peaks spaced 174 ± 20 cm^{-1} apart are rather well pronounced. This interval coincides within the limits of experimental error with the frequency of the $4a_u$ vibration in the D_0 state of naphthalene [14], which is excited in the long-wavelength region of the ZEKE PFI spectrum as well. For the D_1 state, the frequencies of the out-of-plane vibrations are unknown, but in view of the fact that the force fields in the D_0 and D_1 states are close, we assigned the dominant peak in the spectrum to the formation of the $D_1(0°)$ ion in an unexcited vibrational state, and the short-wavelength peak was assigned to the ion in the $D_1(4a_u^1)$ state. This assignment gives a value of 71823 ± 30 cm^{-1} (8.904 ± 0.004 eV) for the adiabatic energy of ionization of a naphthalene molecule with production of an ion in the D_1 state. This value falls in the range of less accurate values determined by the photoelectron spectroscopy [15–17].

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