Two-color photoionization spectroscopy of jet-cooled nickelocene

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Two-photon ionization of the nickelocene molecules cooled in a supersonic jet was performed for the first time by simultaneous excitation of $(\eta^5\text{-}C_5H_5)_2Ni$ with two tunable nanosecond dye lasers. The one-photon transition from the HOMO to the Rydberg R4p level was used as the initial step of the multiphoton excitation. In a one-color experiment, the conditions were found for generation of the intact molecular ion, $(\eta^5\text{-}C_5H_5)_2Ni^+$, as the only ionic product of the multiphoton ionization. The use of an intense pulse of the second dye laser lead to an increase in the yield of the molecular ion.

Key words: nickelocene, laser spectroscopy, resonance-enhanced multiphoton ionization, Rydberg transitions.

Among the most interesting classes of organometallic compounds are bis(cyclopentadienyl) transition metal complexes Cp_2M.[1,2] Recently, increasing interest in laser-assisted multiphoton processes in these molecules has been expressed. It is stimulated by great prospects for development of excited-state chemistry of metal complexes including laser-assisted chemical vapor deposition of inorganic films and powders[3] and by the possibility of obtaining unique new information on the molecular structure of metallocenes using recently elaborated laser photoionization spectroscopy methods.[4—7] To this end, one must find conditions for multiphoton ionization (MPI) of jet-cooled metal complexes mentioned above by tunable lasers. However, studies on the interaction of ferrocene and nickelocene with nanosecond pulses of dye lasers in the region of valence transitions[8—12] revealed predominance of multiphoton dissociation (MPD) of molecules, which produces neutral metal atoms. By subsequent laser-assisted MPI of these atoms singly charged Fe^+ and Ni^+ ions are generated, being almost exclusive products detectable by mass spectrometry.[8—12] For instance, for nickelocene the $Ni^+ : Cp_2Ni^+$ signal intensity ratio is greater than 170 even if the laser frequency differs from that of the resonance absorption line of Ni atom.[8]

At the same time, earlier studies[13—16] of one-photon electronic absorption spectra of gaseous Cp_2M revealed clearly defined Rydberg p-transitions. This offers the possibility of MPI of metallocenes involving the lowest Rydberg p-level as the first step of multiphoton process. Subsequent ionization can be achieved by a pulse of the laser exciting the Rydberg state. More detailed information on the molecular structure can be obtained by ionizing molecules by a pulse of a second tunable laser.[4—7] This experimental scheme provided good results in studies of ferrocene[17,18] and bis(η^6-benzene)chromium.[19] In this work we first carried out a two-color MPI of jet-cooled nickelocene molecules.

Experimental

The setup used for MPI of nickelocene molecules was described earlier.[20,21] All operations with the metal complex were performed in inert atmosphere or *in vacuo* ($p = 10^{-2}$ Torr). Crystals of Cp_2Ni synthesized following a known procedure[22] and purified by vacuum sublimation were placed in a heated container equipped with an electromagnetic pulsed nozzle. At 80—120 °C and at open nozzle, nickelocene vapors mixed with argon ($p = 10^3$ Torr) entered an evacuated chamber ($p = 10^{-5}$ Torr). Using two conical skimmers, the central portion of the supersonic jet was redirected into an ionization chamber ($p = 10^{-6}$ Torr) where the molecular beam was crossed by two focused laser beams.

Excitation and ionization of Cp_2Ni molecules was attained using two Quanta Ray PDL-1 tunable dye lasers (the dyes employed were rhodamine-6G, pyridine-1, and DCM (Radiant Dyes)) pumped with a Nd : YAG solid-state laser (Quanta Ray DCR1-A). The tuning range of the doubled frequencies of the first laser (L1) corresponded to the Rydberg $3d_{xz,yz}(e_{1g}) \rightarrow R4p_{x,y}(e_{1u})$ band observed in the one-photon absorption spectrum of gaseous nickelocene (34500—36500 cm^{-1}).[13,14,16] The second laser (L2) operated in

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the spectral region 13600—15800 cm^{-1}, thus providing conditions for ionization of the molecules excited by a pulse of the L1 laser. Each of the two lasers, L1 and L2, was characterized by a linewidth of 0.5 cm^{-1} and a pulse duration of 8 ns. The experimental conditions also provided synchronization of pulses of the L1 and L2 lasers at the point of intersection with the molecular beam. The laser intensity was $5 \cdot 10^6$—$5 \cdot 10^7$ (L1) and $1 \cdot 10^8$—$5 \cdot 10^8$ W cm^{-2} (L2). One-color ionization experiments were carried out with L2 laser switched off. Cations produced by photoionization were accelerated in a constant electric field and detected using a time-of-flight mass spectrometer equipped with a multichannel detector, with a resolution, $M/\Delta M$, of 2000. The two-color photoionization spectrum was corrected for the L2 intensity.

Results and Discussion

Two-color two-photon excitation of nickelocene molecule achieved in this work involves a transition of an electron from the e_{1g}* HOMO to the Rydberg $R4p_{x,y}(e_{1u})$ orbital followed by ionization by a pulse of the L2 laser to generate a Cp_2Ni^+ ion in the ground electronic state $^2E_{1g}$.

To produce highest yields of nickelocene molecular ions, the contribution of competing MPD to the overall process must be minimum. One-color irradiation of Cp_2Ni by intense laser pulses ($5 \cdot 10^7$ W cm^{-2}, laser L1) in the region of resonance absorption lines of neutral Ni atom causes predominance of Ni^+ ions in the mass spectra. In this case, it is quite easy to obtain the mass spectra exhibiting exclusively Ni^+ peaks, which is consistent with the published data on MPD of nickelocene.[8—12] At the same time even under these conditions the increase in the concentration of Cp_2Ni molecules in the beam by heating the sample from 80 to 120 °C and a decrease in the L1 laser intensity by defocusing the laser beam cause the appearance of molecular ion peaks from Cp_2Ni^+ and fragment ion peaks from $CpNi^+$ with the intensities comparable with those of the Ni^+ peaks (Fig. 1, spectrum *a*).

The signals were identified on the basis of both the m/z values and the isotopic structure. The Ni^+ ion is characterized by two strong peaks at m/z 58 and 60 and by weak peaks at m/z 61 and 62, which is consistent with the natural abundance (^{58}Ni, 68.27%; ^{60}Ni, 26.10%; ^{61}Ni, 1.13%; ^{62}Ni, 3.59%).[23] Analogous peaks are also observed in the structure of the signal of Cp_2Ni^+, namely, strong peaks at m/z 188 and 190 ($^{12}C_{10}{}^1H_{10}{}^{58}Ni^+$, $^{12}C_{10}{}^1H_{10}{}^{60}Ni^+$) and weak peaks at m/z 191 and 192 ($^{12}C_{10}{}^1H_{10}{}^{61}Ni^+$, $^{12}C_{10}{}^1H_{10}{}^{62}Ni^+$). Additionally, the mass spectrum exhibits a clearly seen peak of $^{12}C_9{}^{13}C_1{}^1H_{10}{}^{58}Ni^+$ ions at m/z 189. A signal of the $CpNi^+$ fragment ion is weaker than the signals of Cp_2Ni^+ and Ni^+ (see Fig. 1, spectrum *a*); however, the peaks at m/z 121 ($^{12}C_5{}^1H_5{}^{58}Ni^+$) and 123 ($^{12}C_5{}^1H_5{}^{60}Ni^+$) are clearly seen.

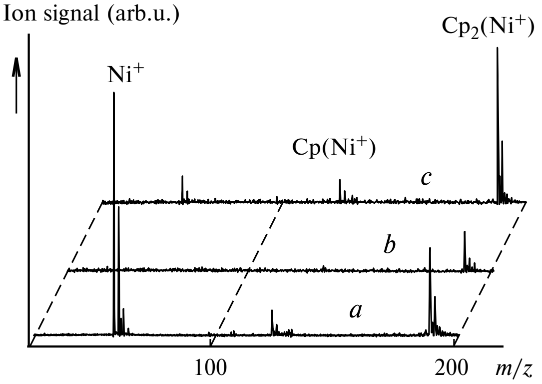

Fig. 1. Photoionization mass spectra of jet-cooled nickelocene at the one-color (*a*, *b*) and two-color (*c*) excitation. The laser wavenumbers are ν_{L1} = 35434 (*a*) and 35710 cm^{-1} (*b*, *c*) and ν_{L2} = 15090 cm^{-1} (*c*) and the laser intensities are I_{L1} = 10 (*a*) and 7 MW cm^{-2} (*b*, *c*) and I_{L2} = 300 MW cm^{-2} (*c*). The laser wavenumber ν_{L1} = 35434 cm^{-1} corresponds to the resonance absorption line of Ni atom at 282.1 nm.[23]

The relative intensities of the Cp_2Ni^+ peaks increase if the L1 laser frequency L1 differs from that of the resonance absorption line of Ni^I. This is associated with a decrease in the efficiency of ionization of Ni atom with the L1 pulse. In this case it is possible to obtain a mass spectrum exhibiting only molecular ion peaks (see Fig. 1, spectrum *b*). Only Ni^+ ions were detected in all the preceding studies of the interaction of Cp_2Ni molecules with laser radiation.[8,10]

Generation of Cp_2Ni^+ cations in one-color irradiation of nickelocene points that highly efficient MPI can be achieved even if nickelocene interacts with nanosecond laser pulses. Two-color excitation requires that the parameters of the L2 laser pulse be chosen in such a way that the Cp_2Ni^+ signal be substantially amplified (see Fig. 1, spectrum *c*). The action of the L2 laser pulse on Cp_2Ni molecules with the laser L1 switched off does not produce ions. Therefore, the observed increase in the signal intensity of molecular ions is governed exclusively by the two-color process. The isotopic structure of the signals in the two-color mass spectrum exactly matches the isotopic structure observed in the one-frequency spectrum. The appearance of the two-color signal of Cp_2Ni^+ in the photoionization mass spectrum (see Fig. 1, spectrum *c*) opens up the possibility of using multiphoton laser spectroscopy to study the properties of nickelocene molecule.

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* Here, the MO symmetry types and electronic states of Cp_2Ni are denoted using irreducible representations of the D_{5d} point group.

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