

Photoelectron Spectroscopic Characterization of the Niobium–Benzene Anion Produced by Reaction of Niobium with Ethylene

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Studies of the chemistries of gas phase transition metal atoms, ions, and small clusters have yielded many surprising results.^{1,2} For example, for the simplest unsaturated hydrocarbons, acetylene (C₂H₂) or ethylene (C₂H₄), experimental studies of their reactivities with small metal clusters, such as Fe₄⁺,^{3,4} and even with single metal atoms or ions, such as Fe⁺,^{5,6} Nb⁺,⁷ W⁺,⁸ U⁺,⁹ and supported Pd,¹⁰ have indicated the formation of metal-bound benzene. These experiments have employed mass spectrometric methods, such as collision-induced dissociation, as the structural probe. Here, we report direct *spectroscopic* evidence of the metal–benzene structure for NbC₆H₆[−] anions produced upon reaction with ethylene.

In our apparatus,¹¹ anions are prepared in a flowing afterglow reactor, mass selected, and probed by photoelectron spectroscopy. In the present experiment, the 5 cm diameter flow tube (Figure 1) incorporated a cold cathode DC discharge source,¹² with a niobium cathode (−2.5 kV, 12 mA) positioned 107 cm from the 2 mm diameter nosecone sampling aperture. Flow rates of the He and Ar buffer gases were 7 and 0.7 SLPM (std. L/min), respectively, giving a flow tube pressure of 0.5 Torr. The initially hot plasma was relaxed by passage through a 30 cm long flow tube section immersed in liquid nitrogen. The anion current was measured by a Faraday cup following the laser crossing in the spectroscopy chamber, 8 feet from the nosecone. A portion of the mass spectrum is shown in Figure 1 (bottom). The most abundant anions are Nb₄[−] and Nb₅[−] (5 pA). Larger bare metal clusters with smaller relative abundances are also detected, as described in our study of Nb₈[−],¹³ and metal carbides and/or oxides are observed. However, virtually no Nb[−] atomic anion (93 amu) is detected.

Ethylene (C₂H₄ or C₂D₄) was introduced at the reactant inlet following the cooled section of the flow tube, as a 2% mixture in Ar added at 1.0 SCCM (std. cm³/min). As illustrated in Figure 1 (top), the mass spectrum obtained upon adding C₂H₄ is dominated by anions containing a single Nb atom, including NbC₂H₂[−] (290 pA), NbC₄H₄[−] (120 pA), NbC₆H₆[−] (45 pA), and NbC₈H₈[−] (30 pA). Substantial retuning of the ion optics following the nosecone was required to reoptimize the anion current, so the comparison of anion intensities before and after ethylene addition is not quantitative. Nevertheless, in view of the scarcity of anions containing just one Nb atom prior to ethylene addition, it is likely that the neutral Nb atom is the major metal-containing reactant for the production of these abundant anions. Previous studies have established that in its 4d⁴ 5s¹ (⁶D) ground state, Nb reacts with C₂H₄ at nearly the estimated hard-spheres collision rate, with no barrier (in excess of the energy of the reactants) to the exothermic elimination of H₂.^{14–17} The higher mass region in Figure 1 (×10) displays weaker intensities of metal cluster carbides and partially dehydrogenated clusters with even numbers of C and of H atoms. No hydrocarbon anions were observed in the <100 amu region.

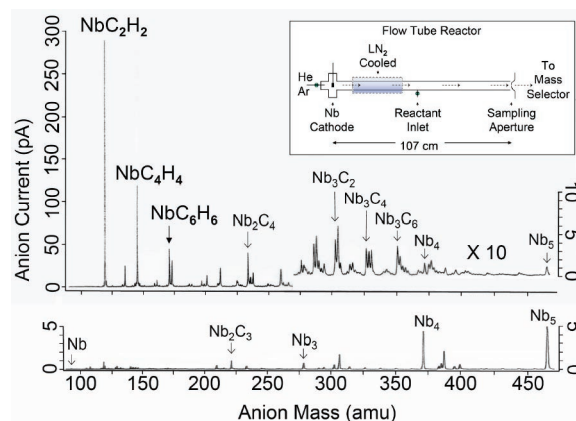


Figure 1. Mass spectra without (bottom) and with (top) addition of ethylene to the flow tube reactor (inset) at the reactant inlet.

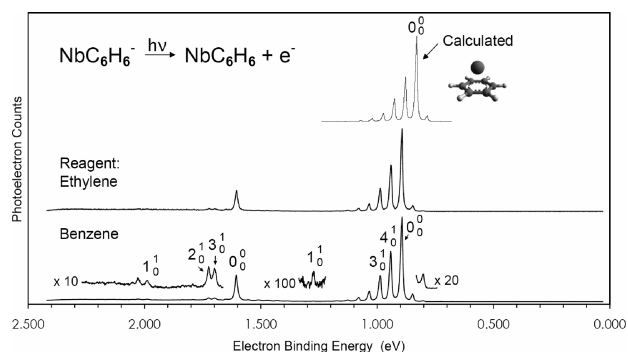


Figure 2. Photoelectron spectra of NbC₆H₆[−] produced upon reaction with ethylene (middle) versus benzene (bottom). Top: calculated spectrum for the ³A₁ → ²A₁ + e[−] photodetachment transition of the C_{6v} Nb–benzene anion.

A portion of the 488 nm photoelectron spectrum of mass-selected NbC₆H₆[−] prepared from C₂H₄ is shown in Figure 2 (middle). The *x*-axis gives the electron binding energy, that is, the photon energy (2.540 eV) minus the measured electron kinetic energy. The spectrum displays vibrationally resolved photodetachment transitions from NbC₆H₆[−] to two electronic states of neutral NbC₆H₆. The position of the origin band in the transition to the lower energy state, which we assign as the ground state, gives an electron affinity (EA) of 0.893 ± 0.006 eV for NbC₆H₆. This value is close to the 0.916 ± 0.005 eV EA that we measure for Nb.

As one test of the NbC₆H₆[−] anion structure, we recorded the photoelectron spectrum of NbC₆H₆[−] prepared by adding benzene (C₆H₆ or C₆D₆, 0.5 SCCM), rather than ethylene, to the flow tube. As shown in Figure 2 (bottom), the resulting spectrum is the same as that obtained for the NbC₆H₆[−] anions produced from ethylene.

The ground state transition in these photoelectron spectra displays three active vibrational modes, with fundamental frequencies of 382 ± 10 (355 ± 10), 740 ± 15 (588 ± 10),¹⁸ and 3060 ± 25 (2310 ± 30) cm^{−1} in neutral NbC₆H₆ (NbC₆D₆). Anion frequencies

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for the former modes are 375 ± 15 (345 ± 10) and 730 ± 20 (565 ± 15) cm^{-1} . For the 740 ± 15 (588 ± 10) mode, consistent values of 748.5 (588.3) cm^{-1} have been measured in matrix IR studies of the neutral molecule prepared from niobium and benzene.¹⁹

To analyze the photoelectron spectra in greater detail, we employed density functional theory (DFT) using the Gaussian²⁰ B3LYP method with the Stuttgart RSC ECP basis set for Nb and 6-311++G(df,pd) for C and H. These calculations found the ground state of the Nb–benzene complex, as depicted in Figure 2, to be 3A_1 for the anion and 2A_1 for the neutral molecule. The spin multiplicities of these complexes are thus reduced from those in bare Nb⁺ [$4d^4 5s^2$, 5D] and Nb [$4d^4 5s^1$ (6D)]. Both complexes are predicted to have essentially C_{6v} symmetry. In the triplet NbC₆H₆[−] ground state, the two unpaired electrons are calculated to have an $(a_1)^1(a_1)^1$ configuration. The doublet NbC₆H₆ ground state is accessed by electron detachment from the a_1 molecular orbital of primarily Nb 5s atomic parentage.

If the anionic and neutral complexes have the same symmetry, then the observed progressions in the photoelectron spectrum must be associated with totally symmetric (A_1) vibrational modes, of which there are four in a C_{6v} Nb–benzene complex. Their intensities in the spectrum will also depend on the differences between the equilibrium geometries of the anion and neutral molecule states. These are calculated to be mainly a lengthening of the distance between the Nb atom and the plane of the carbon ring in the anion (1.76 vs 1.71 Å) and an increase in the C–H bond angle with respect to that plane (2.5 vs 1.3°). Thus, the two corresponding normal modes, the metal–ligand stretch and the out-of-plane hydrogen bend, are expected to be most active in the ground state transition. The geometry displacements are small, consistent with a description of the a_1 highest occupied molecular orbital of the anion as essentially nonbonding.

Figure 2 (top) shows the calculated photodetachment transition to the NbC₆H₆ ground state, based upon the DFT results for the geometries and vibrational properties of the anionic and neutral complexes. This simulation was done with the aid of the Franck–Condon photoelectron spectral analysis programs PESCAL and FCFGAUS.²¹ The calculated EA (0.830 eV) is close to the measured value (0.893 ± 0.006 eV). The predicted vibrational band intensity profiles and peak intervals agree well with experiment, providing additional support for these electronic and vibrational state assignments. The DFT frequencies for the protonated (perdeuterated) complexes are 381 (353) cm^{-1} for the neutral molecule and 369 (341) cm^{-1} for the anion for the symmetric metal–ligand stretch, in excellent agreement with the 382 (355) and 375 (345) cm^{-1} measured values. For the symmetric out-of-plane hydrogen bend, the calculated frequencies are 773 (600) (neutral) and 741 (577) cm^{-1} (anion), as compared with the 740 (588) and 730 (565) cm^{-1} values measured here. The neutral molecule symmetric C–H(D) stretch is calculated to be 3199 (2369) cm^{-1} , close to the 3060 (2310) cm^{-1} measured frequencies.

The excited state of neutral NbC₆H₆ observed in the spectrum is measured to lie 0.713 ± 0.004 eV (5750 ± 30 cm^{-1}) above its ground state. The observed vibrational progressions are weak, again indicating only a small difference between the equilibrium geometry of this state and that of the anion (and neutral molecule) ground states. This NbC₆H₆ state is assigned as the excited 2A_1 state accessed by electron detachment from the other singly occupied a_1 anion orbital, which is of primarily Nb $4d_z^2$ atomic parentage, giving a less intense transition in the 488 nm spectrum. The measured vibrational frequencies are 750 ± 20 (585 ± 15), 955 ± 20 (915 ± 15), and 3090 ± 30 (2320 ± 30) cm^{-1} in this excited state of NbC₆H₆ (NbC₆D₆). These active modes can again be assigned as

totally symmetric (A_1) modes of a C_{6v} Nb–benzene complex, that is, the out-of-plane H(D) bending, C–C stretching (ring breathing), and C–H(D) stretching modes, respectively.

In summary, the photoelectron spectrum of the mass-selected NbC₆H₆[−] anion, prepared by reaction with ethylene in the niobium cold cathode discharge flow tube reactor, provides direct evidence that this product anion has the η^6 Nb–benzene structure. The spectrum provides no evidence for any other isomer of NbC₆H₆[−] under these flow tube conditions. The production of this anion appears to involve the initial reaction of a neutral Nb atom with ethylene, to produce NbC₂H₂ with loss of H₂.

Further insight into a possible formation mechanism is provided by the photoelectron spectra and DFT calculations for NbC₂H₂[−] and NbC₄H₄[−].²² For example, the NbC₂H₂[−] spectrum reveals that two structural isomers of this anion are sampled from the flow tube. On the basis of comparisons of the observed photoelectron spectra with those calculated for various possible structures, the lower EA (0.944 ± 0.006 eV) isomer appears to have a cyclic C_{2v} structure, with a 3A_1 anion ground state and a higher spin, quartet 4A_2 ground state for the neutral complex. Following its production, such as by electron attachment to NbC₂H₂ formed upon reaction of atomic Nb with C₂H₄, this triplet (3A_1) isomer of the NbC₂H₂[−] anion appears well-poised to undergo sequential reactions, with conservation of electron spin, with two additional ethylene molecules (with H₂ loss) to produce the observed triplet (3A_1) ground state of the η^6 Nb–benzene anion.

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