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# Photoelectron imaging spectroscopy of MoC<sup>-</sup> and NbN<sup>-</sup> diatomic anions: A comparative study

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The isoeletronic diatomic MoC<sup>-</sup> and NbN<sup>-</sup> anions have been prepared by laser ablation and studied by photoelectron imaging spectroscopy combined with quantum chemistry calculations. The photoelectron spectra of NbN<sup>-</sup> can be very well assigned on the basis of literature reported optical spectroscopy of NbN. In contrast, the photoelectron spectra of MoC<sup>-</sup> are rather complex and the assignments suffered from the presence of many electronically hot bands and limited information from the reported optical spectroscopy of MoC. The electron affinities of NbN and MoC have been determined to be  $1.450 \pm 0.003$  eV and  $1.360 \pm 0.003$  eV, respectively. The good resolution of the imaging spectroscopy provided a chance to resolve the  $\Omega$  splittings of the  $X^3\Sigma^-$  ( $\Omega = 0$  and 1) state of MoC and the  $X^4\Sigma^-$  ( $\Omega = 1/2$  and 3/2) state of MoC<sup>-</sup> for the first time. The spin-orbit splittings of the  $X^2\Delta$  state of NbN<sup>-</sup> and the  $a^2\Delta$  state of MoC<sup>-</sup> were also determined. The similarities and differences between the electronic structures of the NbN and MoC systems were discussed. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4918589]

# I. INTRODUCTION

Recently, there has been an increasing interest in studying the electronic structures and reactivity of transition metal carbides and nitrides that are important materials or species in the research fields including catalysis, organometallic chemistry, surface science, superconductivity, and astrochemistry.<sup>1–10</sup> In particular, supported molybdenum carbide nano-particles can be active catalysts for methane dehydroaromatization into benzene,<sup>11,12</sup> dehydrogenation of ethane and propane into olefins,<sup>13,14</sup> Fischer-Tropsch synthesis,<sup>15</sup> hydrogen production in electrocatalysis,16 and so on.17 Diatomic metal carbides and nitrides are the simplest systems to understand the chemical bonding and reactivity of related materials. We have studied the reactivity of MoC<sup>+</sup> diatomic cations with methane and the C-H bond activation process has been identified.<sup>3</sup> In contrast, the oxide counterpart MoO<sup>+</sup> was inert with methane. Our recent experimental study indicated that the molybdenum carbide anions were also reactive with hydrocarbon molecules. To understand the observed chemical reactivity, it is important to study the electronic structures of these metal carbide species.

Photoelectron spectroscopy (PES) and its extension of photoelectron imaging spectroscopy (PEIS)<sup>18,19</sup> are important

techniques to probe the electronic structures of gas phase species and provide benchmark data for quantum chemistry calculations. This study reports the PEIS of the  $MoC^-$  anion and its isoeletronic species  $NbN^-$ . It is known that the electronic structures of diatomic carbides can be more complex than those of the diatomic nitrides or oxides.<sup>1</sup> The simpler  $NbN^-$  system may be used as a guide to understand the more complex  $MoC^-$  system.

The photoelectron spectroscopy of MoC<sup>-</sup> with laser excitations at 532 and 355 nm was studied by Wang and his coworkers in 1999.<sup>20</sup> The resonant two-photon ionization (R2PI) and dispersed fluorescence (DF) spectroscopy of neutral MoC molecule was studied by Morse and his coworkers in 1998 and 2001, respectively.<sup>21,22</sup> The permanent electric dipole moment of MoC was measured in 2007 by Steimle and his coworkers.<sup>23</sup> In addition, high-level quantum chemistry calculations with multireference configuration interaction (MRCI) on MoC were performed in 1997 by Shim and Gingerich.<sup>24</sup> Such calculations were also carried out and extended to include MoC<sup>±</sup> ions in 2006 by Denis and Balasubramanian.<sup>25</sup> The electronic ground states of MoC<sup>-</sup> and MoC were determined to be  ${}^{4}\Sigma^{-}$  and  ${}^{3}\Sigma^{-}$ , respectively. The R2PI and DF spectroscopy on  $MoC^{21,22}$  could not determine the splitting of the two  $\boldsymbol{\Omega}$ components of  ${}^{3}\Sigma^{-}$  state ( $\Omega = 0$  and 1), which was estimated to be about 155 cm<sup>-1</sup> by considering a second order spinorbit (SO) effect.<sup>21</sup> It is possible to determine such a splitting by the PEIS that can have sufficient energy resolution.<sup>18,19</sup>

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The first electronically excited state (EES) of MoC, which was computed to be a  ${}^{3}\Delta$  state around 3430–3660 cm<sup>-1</sup>, was measured by the DF spectroscopy at 4002.5 cm<sup>-1</sup> ( ${}^{3}\Delta_{2}$ ) with respect to the X ${}^{3}\Sigma_{-0}$  level. The first EES of MoC<sup>-</sup> was predicted to be a  ${}^{2}\Delta$  state at only 2182 cm<sup>-1</sup>.<sup>25</sup> The electron affinity (EA) of MoC was experimentally determined to be 1.358 eV<sup>20</sup> which was poorly reproduced (1.01 eV) by the quantum chemistry calculations.<sup>25</sup>

The EA of the NbN molecule was measured to be  $1.42 \pm 0.02$  eV by Castleman and his coworkers to differentiate NbN<sup>-</sup> from NbCH<sub>2</sub><sup>-</sup> in mass spectrometric studies.<sup>26</sup> The optical spectroscopy of NbN has been very well studied by Dunn and Rao,<sup>27</sup> Ram and Bernath,<sup>28,29</sup> and others including Féménias and Azuma.<sup>30,31</sup> All of the experimentally determined electronic states of NbN below  $20\,000\,\text{cm}^{-1}\,(\text{X}^3\Delta,$  $a^{1}\Delta$ ,  $A^{3}\Sigma^{-}$ ,  $b^{1}\Sigma^{+}$ ,  $c^{1}\Gamma$ ,  $d^{1}\Sigma^{+}$ ,  $B^{3}\Phi$ ,  $C^{3}\Pi$ , and  $e^{1}\Pi$ ) can be very well interpreted on the basis of the high-level MRCI calculations by Langhoff and Bauschlicher in 1990.32 The SO interaction splits the  ${}^{3}\Delta$  ground state of NbN into  ${}^{3}\Delta_{1}$ ,  ${}^{3}\Delta_{2}$ , and  ${}^{3}\Delta_{3}$  of which the relative energies have been determined by the optical spectroscopy to be at 0, 400.5, and  $891.0 \text{ cm}^{-1}$ , respectively. It is expected that the well determined energy levels of NbN can be used to interpret the PEI spectrum of the anion. The information from the PEIS of NbN<sup>-</sup>, such as the patterns of vibrational progression, the SO multiples, and the photoelectron angular distribution (PAD)<sup>33</sup> for specific electronic transitions can then be used to have a better understanding of the isoelectronic system of MoC<sup>-</sup>.

## **II. METHODS**

#### A. Experimental methods

A tandem reflectron time-of-flight mass spectrometer (TOF-MS) equipped with a laser ablation cluster source and a PEI spectrometer was used in this study. The schematic diagram of the apparatus is shown in Fig. 1. The cluster



FIG. 1. Schematic diagram of the tandem time-of-flight mass spectrometer coupled with the photoelectron imaging system. The parts labeled: 1, laser ablation ion source; 2 and 10, laser beams; 3, electrodes to accelerate ions; 4, deflectors and einzel lens; 5a, 5b, and 8, reflectors; 6, mass gate; 7, einzel lens; 9, dual micro-channel plate detector; 11, electrodes to accelerate and focus electrons; 12, double-layered  $\mu$ -metal; 13, dual micro-channel plate detector and phosphor screen; and 14, charge-coupled device camera.

source (composed with 1 and 2 in Fig. 1) and the TOF-MS system with 3-9 are the same as the ones used previously to study the photo-induced reaction of mass-select cluster ions.<sup>34</sup> The system with 10-14 was built and installed in this study to record the PEI spectra of mass-selected MoC<sup>-</sup> and NbN<sup>-</sup> anions. The MoC<sup>-</sup> anions were generated by laser vaporization of a rotating and translating molybdenum metal disk compressed with isotope-enriched <sup>98</sup>Mo powder (99.45%, Trace Science International) in the presence of 0.5% CH<sub>4</sub> seeded in a He carrier gas with a back pressure of 6 standard atmospheres. Similarly, the NbN<sup>-</sup> anions were generate by using Nb metal disk and 0.1% NH<sub>3</sub> seeded in He. The generated anions passed through two identical reflectors (5a and 5b) with Z-shaped configuration in the primary TOF-MS and then the ions of interest were selected by a mass gate (6) to interact with a wavelength-tunable laser beam (10) delivered from an OPO (optical parametric oscillator, Continuum, Horizon I, 3–7 cm<sup>-1</sup> line width) laser source. The kinetic energies (or velocities) of the photo-detached electrons were measured by the PEI spectrometer similar to the ones described in literature.<sup>18,19</sup> The apparatus can also monitor daughter ions from photo-induced fragmentation by using the secondary reflectron TOF-MS (7–9) as described previously.<sup>34</sup> In this study, no fragmentation of MoC<sup>-</sup> and NbN<sup>-</sup> could be observed. In addition to <sup>98</sup>MoC<sup>-</sup> and NbN<sup>-</sup>, hydrogen containing species including 98MoCH2- and NbNH1,2- were also generated by the cluster source. The TOF-MS is good enough to well resolve these mass peaks and to monitor the mass-selection process to make sure that only <sup>98</sup>MoC<sup>-</sup> or NbN<sup>-</sup> passed through the mass gate to interact with the OPO laser of which the wavelengths were determined using a grating spectrograph (GS, Acton SpectraPro 500I) calibrated with atomic spectral lines of a mercury-argon (Hg-Ar) lamp.<sup>35</sup> The air-wavelengths are given in this paper, and the conversion to vacuum-wavelengths were made with IAU standard.<sup>36</sup>

Each time the OPO laser was tuned to a wavelength (x, to be determined) to record a PEI spectrum, a small portion of the laser light was delivered to the GS so that a wavelength value  $(\lambda)$  could be read. The GS was also run to read the wavelength values  $(\lambda_i)$  of at least two Hg-Ar atomic lines with accurate wavelengths of  $y_i$  (i = 1, 2, ..., N,  $N \ge 2$ ). Our GS was pre-calibrated so that  $|y_i - \lambda_i|$  was small (~1 nm). By using a least-square procedure, the data sets  $(\lambda_i)$  and  $(y_i)$  were used to determine a linear relationship that was then used to calculate x from  $\lambda$ . For example, when N = 2,  $x = y_1 + (\lambda - \lambda_1) \times (y_2 - y_1)/(\lambda_2 - \lambda_1)$ . It is important to note that moving the grating angle back and forth during a set of calibration (reading  $\lambda$  and then  $\lambda_i$ ) should be avoided because the GS wavelength-reading could change slightly  $(\pm 0.2 \text{ nm})$  after a grating moving. However, for each new calibration, the grating angle should be moved to an appropriate position so that  $\lambda$  could be covered by  $(\lambda_i)$ , i.e.,  $\lambda_1 < \lambda < \lambda_N$ . The uncertainties of reading  $\lambda$  and  $\lambda_i$  values were less than 0.02 nm. In the two-line experiment (N = 2), the accuracy of x could be better than  $\pm 0.04$  nm, corresponding to  $\pm 3 \text{ cm}^{-1}$  around 400 nm. Our wavelength calibration did not take into account the non-linearity between  $(\lambda_i)$  and  $(y_i)$ , which was found to be negligible in the multipleline (N > 2) experiments. In practice, we set and calibrated

the OPO laser wavelengths in many different values (covering 355 nm–520 nm) to measure the EA of the Au atom (EA<sub>Au</sub>), which involved additional calibration of the photoelectron kinetic energy (see the text below). The largest deviation between our EA<sub>Au</sub> values and the reported one (2.3090  $\pm$  0.0010 eV)<sup>37</sup> was 2.2 meV.

As shown in Fig. 1, our PEI spectrometer was constructed with an assembly of molybdenum electrodes (11), a doublelayered  $\mu$ -metal shield (12), and the signal generation (13) and detection (14) sub-systems. The photo-detached electrons were accelerated by pulsed-electric potential as high as -2000 V to the detection sub-system 13 assembled with two micro-channel places (MCPs,  $\Phi 50/12$  from Night Vision Technology) and one phosphor screen (PS, PN-40-008 from Beam Imaging Solutions). The electron positions on the PS were imaged with a charge-coupled device (CCD) camera (14, UP680CL from UNIQ). The images were transferred into a computer for averaging (by 10000-50000 laser shots) and inverse-Abel transformation of the two-dimensional (2D) images into three-dimensional (3D) electron distributions as described in literature.<sup>38</sup> The electron kinetic energies  $(E_k)$  or velocities  $(v_e)$  were calibrated using the well determined EA value of gold atom by recording the PEI spectra of Au<sup>-</sup> at several laser wavelengths ranging from 355 to 520 nm (Fig. 2(a)). As shown in Fig. 2(b), there is a very good lineardependence between the  $v_{\rm e}$  values and the radial distributions of the transformed 3D images. The relative energy resolution  $(\Delta E_k/E_k)$  is around 3% (best = 2.6%) at  $E_k$  of about 1.0 eV while it degrades to about 9% at the small  $E_k$  value of 0.1 eV (Fig. 2(c)). The absolute energy resolution ( $\Delta E_k$ ) improves as the kinetic energy decreases. The precision of the absolute electron detachment energies for narrow and unblended bands is better than  $\pm 3$  meV while the precision for the relative energies can be better than  $\pm 1$  meV.

In addition to the photoelectron kinetic energies, the PAD can also be derived from the experimental images. For one-photon detachment, the PAD is given by<sup>33</sup>

$$I(\theta) \sim [1 + \beta P_2(\cos \theta)], \tag{1}$$



in which  $\theta$  is the angle between the direction of the ejected electron and the polarization direction of the detachment laser,  $P_2$  is the second order Legendre polynomial, and  $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ . The anisotropy parameter,  $\beta$ , is encoded with information quantifying the degree of alignment between the direction of the photo-detached electrons and the laser polarization direction, and it is numerically confined as  $-1 \le \beta \le 2$ . To satisfy the dipole selection rule,  $\Delta l = \pm 1$ , the electron detachment from s-type (l = 0) atomic orbital (AO) generate one type  $(s \rightarrow p, l = 0 + 1)$  of outgoing partial wave with maximum intensity parallel to the laser polarization direction and  $\beta = 2$ . The electron detachment from other AO (such as p or d) can generate two types (such as  $p \rightarrow s$  and  $p \rightarrow s$ d; or  $d \to p$  and  $d \to f$ ) of outgoing partial waves and their pure interference can result in  $\beta = -1$ . Without inferences, the  $p \to s, p \to d, d \to p$ , and  $d \to f$  partial waves have the  $\beta$  parameters ranging from 0 to 1. In molecular system, the photoelectron angular distributions can be obtained by calculating the overlap integration of the initial and final wavefunction based on molecular orbitals (MOs).<sup>39,40</sup>

# **B.** Theoretical methods

The *ab initio* calculations using Gaussian 09 program<sup>41</sup> have been carried out to investigate the ground state structures and energies of MoC<sup>-</sup> and NbN<sup>-</sup> ions and their neutral counterparts. The coupled-cluster method with single, double, and perturbative triple excitations method [CCSD(T)]<sup>42,43</sup> was used. The aug-cc-pwCVQZ-PP basis set<sup>44</sup> for Mo and Nb atoms and the aug-cc-pVQZ basis set<sup>45</sup> for C and N atoms were adopted. The 4s4p electrons of Mo and Nb were correlated in all the coupled-cluster calculations. Meanwhile, the scalar relativistic effect was taken into account using the Stuttgart new relativistic energy-consistent small-core pseudopotential (PP) ECP28MDF in combination with the above basis set for Mo and Nb.<sup>44</sup> The bond lengths of the diatomic systems were scanned to get the minimum energies.

To calculate the SO splitting of the  $^{2}\Delta$  states ( $^{2}\Delta_{3/2}$  and  $^{2}\Delta_{5/2}$  components) of the MoC<sup>-</sup> and NbN<sup>-</sup> anions,

FIG. 2. Test (a), calibration (b), and resolution (c) of the photoelectron imaging system. The raw images of Au<sup>-</sup> ions taken at 355 and 520 nm are shown on the top left and the corresponding photoelectron spectra are given in (a). The linear relationship between photoelectron velocities and size of the image on the micro-channel plate detector is shown in (b). Panel (c) shows the absolute (hollow circles,  $\Delta E_k$  is defined as full width at half maximum, vertical axis on the left) and relative (solid circles,  $\Delta E_k/E_k$ , vertical axis on the right) energy resolutions in terms of electron kinetic energies  $(E_k)$ .

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the Multiconfiguration reference internally contracted configuration interaction (MRCISD) calculations<sup>46</sup> with Molpro program package<sup>47</sup> were performed. The basis sets and pseudopotentials used were the same as those in the CCSD(T) calculations. The 4s4p electrons of Mo and Nb were correlated in all the MRCISD calculations. The MRCISD and the preceding complete active space self-consistent field (CASSCF) calculations employed an active space composed of full valence shells of Mo/Nb and C atoms, i.e., Mo/Nb 4d, 5s, and C/N 2s, 2p orbitals, for distributing all valence electrons of MoC<sup>-</sup> and NbN<sup>-</sup>. This resultant active space is thus 11 electrons distributed in 10 orbitals, labeled as (11e, 10o). The SO coupling effect was included using a contracted SO configuration interaction method<sup>48</sup> with two-component SO PPs<sup>44</sup> on transition metals. Only two degenerate  $^{2}\Delta$  states were included in the SO coupling state-interacting calculations. The SO coupling matrix was constructed on a basis of the MRCISD state-specific scalar relativistic states. The matrix was then diagonalized to obtain the SO states and energies.

# **III. RESULTS**

# A. Experimental spectra and assignments

# 1. The NbN system

The PE images and the transformed spectra in terms of electron binding energy (BE) at two typical excitation laser wavelengths are shown in Fig. 3 for NbN<sup>-</sup>. The observed BEs and the  $\beta$  parameters are collected in Table I. The spectrum of NbN<sup>-</sup> in Fig. 3(a) shows that a strong and sharp band, marked as X<sub>1</sub>, is located at 1.450 ± 0.003 eV, which can be assigned as the EA defining transition of NbN. This assignment is also supported by the computational result in Subsection III B below. Slightly above the X<sub>1</sub> band, three additional bands, marked as X<sub>i</sub> (*i* = 2–4), were observed. All of the four X bands have similar  $\beta$  parameters, indicating that these bands



FIG. 3. Photoelectron images and spectra taken at 550 nm (a) and 405 nm (b) for NbN<sup>-</sup>. The weak and narrow peaks between  $a_2$  and  $\gamma$  bands in panel (b) are due to noises.

have the same or similar electronic excitation. The  $X_1/X_2$ doublet has a splitting of 395 ± 8 cm<sup>-1</sup>, which is very close to the literature reported SO splitting of NbN ground state  $X^3\Delta$  ( $^3\Delta_2 - {}^3\Delta_1$  splitting of 400.5 cm<sup>-1</sup>).<sup>30</sup> The  $X_3/X_4$  doublet has a slightly smaller splitting of 371 ± 8 cm<sup>-1</sup>. The  $X_1-X_3$ and  $X_2-X_4$  distances (1049 and 1025 cm<sup>-1</sup>) are very close to the ground state vibrational frequency of NbN, 1034 cm<sup>-1</sup> defined as the energy difference between  $X^3\Delta_2$  (v = 1) and  $X^3\Delta_2$  (v = 0) states by optical spectroscopy.<sup>29</sup> As a result, the first four sharp bands of NbN<sup>-</sup>,  $X_i$  (i = 1-4), can be very well assigned (see Table I). It turns out that the  $X^3\Delta_1$  component can have a slightly larger vibrational frequency of 1049 ± 8 cm<sup>-1</sup> than that of  $X^3\Delta_2$  (1025 ± 8 cm<sup>-1</sup> by this work and 1034 cm<sup>-1</sup> by Ref. 29).

The ground state of NbN has the electron configuration of  $(3\sigma)^1(1\delta)^{1,32}$  To form NbN<sup>-</sup>, the additional electron occupies the  $3\sigma$  rather than the  $1\delta$  orbital of NbN, resulting in the  $^2\Delta[(3\sigma)^2(1\delta)^1]$  rather than the  $^4\Sigma^-[(3\sigma)^1(1\delta)^2]$  ground

TABLE I. Observed BEs,  $\beta$  parameters, and assignments for NbN.

		As	Upper state $E$ (cm <sup>-1</sup> )			
Label	BE (eV)	$\beta/\lambda$ (nm)	Electronic	Vibrational	This work	Reference
hb	1.333		${}^{3}\Delta_{1} \leftarrow {}^{2}\Delta_{3/2}$	$0 \leftarrow 1$		
α	1.388		${}^{3}\Delta_{2} \leftarrow {}^{2}\Delta_{5/2}$	$0 \leftarrow 0$		
$X_1$	1.450	2.0/550	${}^{3}\Delta_{1} \leftarrow {}^{2}\Delta_{3/2}$	$0 \rightarrow 0$	0	0
$X_2$	1.499	1.9/550	${}^{3}\Delta_{2} \leftarrow {}^{2}\Delta_{3/2}$	$0 \rightarrow 0$	395	400.5 <sup>a</sup>
X3	1.580	2.0/550	${}^{3}\Delta_{1} \leftarrow {}^{2}\Delta_{3/2}$	$1 \leftarrow 0$	1 049	
$X_4$	1.626	1.9/550	${}^{3}\Delta_{2} \leftarrow {}^{2}\Delta_{3/2}$	$1 \leftarrow 0$	1 4 2 0	1434.6 <sup>b</sup>
β	1.982	1.3/550	$^{1}\Delta_{2} \leftarrow ^{2}\Delta_{5/2}$	$0 \leftarrow 0$		
		1.6/405				
a <sub>1</sub>	2.093	0.7/550	$^{1}\Delta_{2} \leftarrow ^{2}\Delta_{3/2}$	$0 \rightarrow 0$	5 186	5197.4 <sup>a</sup>
a <sub>2</sub>	2.225	0.5/550	$^{1}\Delta_{2} \leftarrow ^{2}\Delta_{3/2}$	$1 \leftarrow 0$	6 2 5 1	6260.6 <sup>c</sup>
А	2.142	0.5/550	${}^{3}\Sigma_{1}^{-} \leftarrow {}^{2}\Delta_{3/2}$	$0 \rightarrow 0$	5 581	5604.5 <sup>a</sup>
b	2.176	0.6/550	$^{1}\Sigma_{0}^{+} \leftarrow ^{2}\Delta_{3/2}$	$0 \rightarrow 0$	5 856	5862.8 <sup>a</sup>
γ	2.570	0.5/405	$^{1}\Gamma_{4} \leftarrow ^{2}\Delta_{5/2}$	$0 \leftarrow 0$		
c <sub>1</sub>	2.681	0.4/405	${}^{1}\Gamma_{4} \leftarrow {}^{2}\Delta_{3/2}$	$0 \leftarrow 0$	9 929	9912.9 <mark>a</mark>
C2	2.806	0.5/405	${}^{1}\Gamma_{4} \leftarrow {}^{2}\Delta_{3/2}$	$1 \leftarrow 0$	10937	

<sup>b</sup>Reference 29. <sup>c</sup>Reference 28.

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state. This electron occupation is supported by the fact that the  $X_i$  (i = 1-4) bands essentially have the  $\beta$  parameters close to 2.0, which can only be defined by an s-type electron detachment  $[(3\sigma)^1(1\delta)^1 \leftarrow (3\sigma)^2(1\delta)^1]$ . The quantum chemistry calculations in Subsection III B below also predict the same assignment for the electronic ground state of NbN<sup>-</sup>.

Once the X bands  $(X_1-X_4)$  of NbN<sup>-</sup> are assigned, it is straight forward to assign the higher-lying PEI bands on the basis of the NbN energy levels that have been well determined by optical spectroscopy.<sup>28,31</sup> The  $0 \leftarrow 0$  bands of the  $a^1\Delta_2 \leftarrow X^2\Delta_{3/2}$ ,  $A^3\Sigma_1^- \leftarrow X^2\Delta_{3/2}$ ,  $b^1\Sigma_0^+ \leftarrow X^2\Delta_{3/2}$ ,  $c^{1}\Gamma_{4} \leftarrow X^{2}\Delta_{3/2}$  transitions are located at 2.093 ± 0.003 eV,  $2.142 \pm 0.003 \text{ eV}$ ,  $2.176 \pm 0.003 \text{ eV}$ , and  $2.681 \pm 0.003 \text{ eV}$ , respectively. The energy levels of neutral NbN defined by these PEI bands are close to those determined by optical spectroscopy within 24 cm<sup>-1</sup>. The weak  $1 \leftarrow 0$  bands of  $a^1\Delta_2 \leftarrow X^2\Delta_{3/2}$  and  $c^1\Gamma_4 \leftarrow X^2\Delta_{3/2}$  were also observed. The determined vibrational frequency of the  $a^1\Delta_2$  state is 1065  $\pm$  8 cm<sup>-1</sup> which is consistent with the value of 1063.2 cm<sup>-1</sup> by optical spectroscopy.<sup>28</sup> The  $c^1\Gamma_4$  state has a vibrational frequency of  $1008 \pm 8 \text{ cm}^{-1}$ . The observed transitions are all due to excitation of the non-bonding MO of  $3\sigma$  or  $1\delta$ , which only changes the Nb–N bond length slightly. As a result, none of the electronic transition has a long vibrational progression and the determined vibrational frequencies are very close to each other  $(1008-1065 \text{ cm}^{-1})$ .

In addition to the well assignable cold bands of NbN<sup>-</sup>, four weak bands marked as hb,  $\alpha$ , and  $\beta$  in Fig. 3(a), and  $\gamma$  in Fig. 3(b) shall be assigned as hot bands. The hb band at  $1.333 \pm 0.003$  eV can be assigned as vibrationally hot band  $X^{3}\Delta_{1} \leftarrow X^{2}\Delta_{3/2}$  (0  $\leftarrow$  1), which defines the vibrational frequency of NbN<sup>-</sup> at 944 ± 16 cm<sup>-1</sup>. The  $X^{3}\Delta_{2} \leftarrow X^{2}\Delta_{3/2}$  $(0 \leftarrow 1)$  transition could be around the position marked with  $\alpha$  while this  $\alpha$  band is stronger than the hb band, which is not expected because the  ${}^{3}\Delta_{2}$  components are weaker than the  ${}^{3}\Delta_{1}$  ones in the X bands. This implies that additional excited state other than  $X^2\Delta_{3/2}$  (v = 1) could be populated in the experiment. The most possible candidate can be the SO component of  $X^2\Delta_{5/2}$ . The transition from  $X^2\Delta_{5/2}$  can also be used to assign the  $\beta$  and  $\gamma$  bands. It is noteworthy these two bands cannot be assigned as the vibrationally hot bands of the  $a_1$  and  $c_1$  transitions because of the following three considerations: (1) the  $0 \leftarrow 1$  hot bands should not be stronger that the corresponding  $1 \leftarrow 0$  cold bands at  $a_2$  and  $c_2$ , (2) both the  $a_1-\beta$  and  $c_1-\gamma$  distances are  $895 \pm 8 \text{ cm}^{-1}$  which are significantly smaller than the NbN<sup>-</sup> vibrational frequency of 944  $\pm$  16 cm<sup>-1</sup> defined by the hb band, and (3) the  $\beta$  parameter of the  $\beta$  band ( $\beta = 1.3$ ) is significantly larger than that of the  $a_1$  band ( $\beta = 0.7$ ). As assigned in Table I, the weak  $\alpha$ ,  $\beta$ , and  $\gamma$  bands were due to transitions from the X<sup>2</sup> $\Delta_{5/2}$  level that is located at  $895 \pm 8 \text{ cm}^{-1}$  (0.111 ± 0.001 eV) with respect to the  $X^2 \Delta_{3/2}$  ground state.

### 2. The MoC system

The PE images and the transformed spectra at four typical excitation laser wavelengths are shown in Fig. 4 for MoC<sup>-</sup>. The observed BEs and the  $\beta$  parameters are collected in Table II. It turns out that the MoC<sup>-</sup> spectra are much more



FIG. 4. Photoelectron images and spectra taken at 950 nm (a), 600 nm (b), 500 nm (c), and 425 nm (d) for  $MoC^-$ . The inset in (a) shows the expanded spectrum of (a) and the inset in (b) shows the  $X_1$  band taken at 880 nm.

complex than the NbN<sup>-</sup> spectra. The strong X<sub>1</sub> band shown in Fig. 4(b) (600 nm excitation) is the EA defining band of MoC, which should be the  $X^{3}\Sigma^{-}[(1\delta)^{2}] \leftarrow X^{4}\Sigma^{-}[(3\sigma)^{1}(1\delta)^{2}]$ transition from the previous experimental and computational studies on the ground states of MoC and MoC<sup>-.21,24,25</sup> At 880 nm excitation (Fig. 4(b)-inset), this X<sub>1</sub> band can be resolved to have three sub-bands spacing by about 10 meV (~80 cm<sup>-1</sup>). They can be assigned as the  $\Omega$  spittings of the  $\Sigma \leftarrow \Sigma$  transition:  ${}^{3}\Sigma_{0}^{-} \leftarrow {}^{4}\Sigma_{1/2}^{-}$  (X<sub>1</sub>-1 band at 1.360  $\pm 0.003 \text{ eV}$ ),  ${}^{3}\Sigma_{1}^{-} \leftarrow {}^{4}\Sigma_{3/2}^{-}$  (X<sub>1</sub>-2 band at 1.370  $\pm 0.003 \text{ eV}$ ), and  ${}^{3}\Sigma_{1}^{-} \leftarrow {}^{4}\Sigma_{1/2}^{-}$  (X<sub>1</sub>-3 band at 1.380 ± 0.003 eV). The EA of MoC  $(1.360 \pm 0.003 \text{ eV})$  by this PEIS study is in good agreement with the value  $(1.358 \pm 0.010 \text{ eV})$  by the previous PES study.<sup>20</sup> The  $X^{3}\Sigma_{1}^{-} - X^{3}\Sigma_{0}^{-}$  and  $X^{4}\Sigma_{3/2}^{-}$  $-X^{4}\Sigma_{1/2}^{-}$  splittings can be determined to be  $161 \pm 16 \text{ cm}^{-1}$ and  $80 \pm 16$  cm<sup>-1</sup>, respectively. The  $161 \pm 16$  cm<sup>-1</sup> value is very well in agreement with the estimated  $X^{3}\Sigma_{1}^{-} - X^{3}\Sigma_{0}^{-}$ splitting of 155 cm<sup>-1</sup> for MoC by the second order SO effect.<sup>21</sup> The  $X^4 \Sigma_{3/2}^- - X^4 \Sigma_{1/2}^-$  splitting of  $80 \pm 16$  cm<sup>-1</sup> for MoC<sup>-</sup> is also reasonable taking into account that similar splitting (86 cm<sup>-1</sup>) was determined for the  $X^{4}\Sigma^{-}$  state of the isoelectronic system, MoN.49

The X<sub>1</sub> and X<sub>2</sub> bands shown in Fig. 4(b) have similar  $\beta$ parameters (1.0–1.1) and the X<sub>1</sub>–X<sub>2</sub> distance is 1024  $\pm$  24 cm<sup>-1</sup>, which matches the X<sup>3</sup>Σ<sub>0</sub><sup>-</sup>(v = 1) – X<sup>3</sup>Σ<sub>0</sub><sup>-</sup>(v = 0) distance (1000.4 cm<sup>-1</sup>) by the optical spectroscopy.<sup>21</sup> As a result, the X<sub>2</sub> band can be assigned as X<sup>3</sup>Σ<sub>0</sub><sup>-</sup>  $\leftarrow$  X<sup>4</sup>Σ<sub>1/2</sub><sup>-</sup> (1  $\leftarrow$  0). The  $\delta_1$  band almost overlaps with the X<sub>2</sub> band and the former has a larger  $\beta$  parameter than the latter (1.4 versus 1.1 at 600 nm). The relative intensities of the  $\delta$  bands ( $\delta_{1-4}$ ) as well as others including  $\alpha$ ,  $\beta$ , and  $\gamma$  with respect to the intensities of the two X bands were strongly dependent on the source conditions, so the  $\alpha$ – $\delta$  are electronically or vibrationally hot bands. The four  $\delta$  bands of MoC<sup>-</sup> in Fig. 4(c) have very similar

Label	BE (eV)	$eta/\lambda$ (nm)	Assignments		Upper state $E$ (cm <sup>-1</sup> )	
			Electronic	Vibrational	This work	Reference
α	0.909	1.1/950	?			
	0.942	0.5/950	${}^{3}\Sigma_{0}^{-} \leftarrow {}^{2}\Delta_{5/2}$ ?	$0 \leftarrow 0$		
	0.960	0.4/950	${}^{3}\Sigma_{1}^{-} \leftarrow {}^{2}\Delta_{5/2}$ ?	$0 \leftarrow 0$		
	0.986	0.3/950	?			
β	1.107	0.6/880	${}^{3}\Sigma_{1}^{-} \leftarrow {}^{2}\Delta_{3/2}$	$0 \leftarrow 0$		
		1.1/600				
γ	1.249	1.1/880	?			
		1.4/600				
X1-1	1.360	1.0/600	${}^{3}\Sigma_{0}^{-} \leftarrow {}^{4}\Sigma_{1/2}^{-}$	$0 \leftarrow 0$	0	
X1-2	1.370		${}^{3}\Sigma_{1}^{-} \leftarrow {}^{4}\Sigma_{3/2}^{-}$	$0 \leftarrow 0$		
X1-3	1.380		${}^{3}\Sigma_{1}^{-} \leftarrow {}^{4}\Sigma_{1/2}^{-}$	$0 \leftarrow 0$	161	
$X_2$	1.487	1.1/600	${}^{3}\Sigma_{0}^{-} \leftarrow {}^{4}\Sigma_{1/2}^{-}$	$1 \leftarrow 0$	1024	1000.4 <sup>a</sup>
$\delta_1$	1.527	1.4/600	${}^{3}\Delta_{1} \leftarrow {}^{2}\Delta_{3/2}$	$0 \leftarrow 0$	3549	
		1.6/500	/-			
$\delta_2$	1.588	1.4/500	${}^{3}\Delta_{2} \leftarrow {}^{2}\Delta_{3/2}$	$0 \leftarrow 0$	4041	4002 <sup>a</sup>
$\delta_3$	1.652	1.7/500	$^{3}\Delta_{1} \leftarrow ^{2}\Delta_{3/2}$	$1 \leftarrow 0$	4557	
$\delta_4$	1.713	1.4/500	$^{3}\Delta_{2}\leftarrow^{2}\Delta_{3/2}$	$1 \leftarrow 0$	5049	
A <sub>1</sub>	1.789	1.2/500	${}^{3}\Delta_{1} \leftarrow {}^{4}\Sigma_{3/2}^{-}$	$0 \leftarrow 0$	3540	
A <sub>2</sub>	1.851	1.0/500	${}^{3}\Delta_{2} \leftarrow {}^{4}\Sigma_{3/2}^{-}$	$0 \leftarrow 0$	4040	
A <sub>3</sub>	1.926	1.0/500	${}^{3}\Delta_{3} \leftarrow {}^{4}\Sigma_{3/2}^{-}$	$0 \leftarrow 0$	4645	
ε	1.837	0.5/600	${}^{1}\Gamma_{4} \leftarrow {}^{2}\Delta_{5/2}$ ?	$0 \leftarrow 0$		
ζ	1.969	0.1/600	${}^{1}\Gamma_{4} \leftarrow {}^{2}\Delta_{3/2}$ ?	$0 \leftarrow 0$		
a <sub>1</sub>	2.064	1.3/425	${}^5\Sigma^- \leftarrow {}^4\Sigma^-$	$0 \leftarrow 0$	5678 <sup>b,c</sup>	5676 <sup>d</sup>
a <sub>2</sub>	2.196	0.9/425	${}^{5}\Sigma^{-} \leftarrow {}^{4}\Sigma^{-}$	$1 \leftarrow 0$	6743 <sup>b,c</sup>	
η	2.138	0.9/425	${}^{1}\Gamma_{4} \leftarrow {}^{4}\Sigma^{-}$	$0 \leftarrow 1$		
b <sub>1</sub>	2.253	0.6/425	${}^{1}\Gamma_{4} \leftarrow {}^{4}\Sigma^{-}$	$0 \rightarrow 0$	7203 <sup>c</sup>	7647 <sup>d</sup>
b <sub>2</sub>	2.372	0.7/425	${}^{1}\Gamma_{4} \leftarrow {}^{4}\Sigma^{-}$	$1 \leftarrow 0$	8163 <sup>c</sup>	
c	2.365	1.2/500	$^{1}\Delta_{2} \leftarrow {}^{4}\Sigma^{-}$	$0 \rightarrow 0$	8106 <sup>c</sup>	7834 <sup>a</sup>
						8198 <sup>d</sup>
d	2.431	0.9/425	${}^{5}\Pi \leftarrow {}^{4}\Sigma^{-}$ ?	$0 \rightarrow 0$	8638 <sup>b,c</sup>	8740 <sup>d</sup>
	2.461	0.8/425	${}^{5}\Pi \leftarrow {}^{4}\Sigma^{-}$ ?	$0 \rightarrow 0$	8880 <sup>b,c</sup>	
	2.475	0.8/425	${}^{5}\Pi \leftarrow {}^{4}\Sigma^{-}$ ?	$0 \rightarrow 0$	8993 <sup>b,c</sup>	
e	2.587	0.6/425	${}^{1}\Sigma_{0}^{+} \leftarrow {}^{4}\Sigma^{-}$ ?	$0 \rightarrow 0$	9897°	9787 <sup>d</sup>
f	2.692	0.3/425	?			
g	2.799	0.3/425	?			

TABLE II. Observed BEs,  $\beta$  parameters, and assignments for MoC.

<sup>a</sup>Reference 21.

<sup>b</sup>The  $\Omega$  splitting of the  ${}^{4}\Sigma^{-}$  state is not taken into account.

<sup>c</sup>The  ${}^{5}\Sigma^{-}$  or  ${}^{5}\Pi^{-}$  state has additional  $\Omega$  splitting.

<sup>d</sup>Reference 25.

pattern to the four X bands of NbN<sup>-</sup> in Fig. 3(a) in terms of band spacing and relative intensity, so similar assignments, i.e.,  $A^{3}\Delta_{1,2} \leftarrow a^{2}\Delta_{3/2}$  (0  $\leftarrow$  0 and 1  $\leftarrow$  0) can be made (see Table II). Since the  $a^2\Delta_{3/2}$  state of MoC<sup>-</sup> was populated in the experiment to cause quite strong  $A^3\Delta_{1,2} \leftarrow a^2\Delta_{3/2}$  bands, the  $X^{3}\Sigma^{-} \leftarrow a^{2}\Delta_{3/2}$  transition should be observable. The  $\beta$ band is located to the red side of the  $X_1$ -3 band by 0.273 ±  $0.003 \text{ eV} (2202 \pm 24 \text{ cm}^{-1})$  which is very close to the predicted term value of 0.270 eV (2182 cm<sup>-1</sup>) for the energy of  $a^2\Delta$ state of MoC<sup>-.25</sup> As a result, the  $\beta$  band is assigned as the  $X^4\Sigma_1^- \leftarrow a^2\Delta_{3/2}$  transition. When the energy of the  $a^2\Delta_{3/2}$  state is determined (2202 ± 24 cm<sup>-1</sup>), the  $A^{3}\Delta_{1,2} \leftarrow a^{2}\Delta_{3/2}$  transitions then define the energies of  $A^3\Delta_1$  and  $A^3\Delta_2$  with respect to the  $X^{3}\Sigma_{0}^{-}$  ground state to be  $3549 \pm 24$  cm<sup>-1</sup> and 4041 $\pm$  24 cm<sup>-1</sup>, respectively. The 4041  $\pm$  24 cm<sup>-1</sup> value matches the  $A^{3}\Delta_{2}$ - $X^{3}\Sigma_{0}^{-}$  distance of 4002 cm<sup>-1</sup> reported by the optical spectroscopy.<sup>21</sup> In addition, both the  $\delta_1$ - $\delta_3$  and  $\delta_2$ - $\delta_4$  distances

are  $1008 \pm 24 \text{ cm}^{-1}$ , which well matches the reported distance of  $1000.3 \text{ cm}^{-1}$  for  $A^3 \Delta_2(v = 1) - A^3 \Delta_2(v = 0)$  of MoC.<sup>21</sup> The  $\alpha$  bands (Fig. 1(a)-inset) are due to transitions from further high electronic levels of MoC<sup>-</sup>. On the basis of the MRCI calculations on the SO splitting of  $a^2 \Delta_{5/2} - a^2 \Delta_{3/2}$  in this study (see Subsection III B below), the  $\alpha$  bands around 0.94–0.96 eV may be assigned to  $X^4 \Sigma_{0,1}^- \leftarrow a^2 \Delta_{5/2}$ , which determines the term value of  $a^2 \Delta_{5/2}$  to be 3388 ± 80 cm<sup>-1</sup>.

The distance between the  $(X_1-1)$  band and the  $\gamma$  band is 895 cm<sup>-1</sup>, so the  $\gamma$  band might be assigned as vibrationally hot band  $X^3\Sigma^- \leftarrow X^4\Sigma^-$  (0  $\leftarrow$  1). However, because of the following three reasons, this assignment can not be made. (1) The  $\gamma$  band is too strong and it can be even stronger than the  $X_2$  band that is well assigned as  $X^3\Sigma^ \leftarrow X^4\Sigma^-$  (1  $\leftarrow$  0). The 0  $\leftarrow$  1 transition (hot band) should be weaker than the 1  $\leftarrow$  0 transition (cold band) for a diatomic molecule because these two transitions usually have similar Frank-Condon factors while the former is unfavorable in terms of lower state Boltzmann population. (2) At high resolution (Fig. 4(a)-inset, 950 nm excitation), the  $\gamma$  band does not show the sub-bands as observed for the X<sub>1</sub> band (Fig. 4(b)-inset). (3) At 600 nm excitation, the  $\beta$  parameter of the  $\gamma$  band ( $\beta = 1.4$ ) is significantly larger than that of the X<sub>1</sub> band ( $\beta = 1.1$ ). As a result, a high EES of MoC<sup>-</sup> with the minimum term value of 4444 cm<sup>-1</sup> ( ${}^{3}\Delta_{1} \leftarrow ?$ ) can be responsible for the  $\gamma$  band.

At 500 nm excitation (Fig. 4(c)), above the four  $\delta$  bands, three weak bands marked as  $A_{1-3}$  at 1.789  $\pm$  0.003 eV, 1.851  $\pm$  0.003 eV, and 1.926  $\pm$  0.003 eV were observed. They can be assigned as the  $A^3\Delta_{1-3} \leftarrow X^4\Sigma^-$  transition. Their weak intensities suggest that the lower state of the  $A_{1-3}$  bands can be the  $X^4\Sigma_{3/2}^-$  component with the term value of 80 cm^{-1} (Fig. 4(b)-inset). Then, the  $A_{1,2}$  bands define the  $A^3\Delta_1$  energy of 3540  $\pm$  24 cm^{-1} and the  $A^3\Delta_2$  energy of 4040  $\pm$  24 cm^{-1}, which match the term values of the  $A^3\Delta_{1,2}$  states (3549 and 4041 cm^{-1}) defined by the  $\delta_{1,2}$  bands very well.

The PEI bands of  $MoC^-$  (Figs. 4(c) and 4(d)) above the A<sub>1-3</sub> bands can be tentatively assigned on the basis of the previous MRCI calculations.<sup>25</sup> The second and third EESs of MoC predicted by the MRCI are  $a^{5}\Sigma^{-}[(2\sigma)^{1}(3\sigma)^{1}(1\delta)^{2}]$  and  $b^{1}\Gamma[(1\delta)^{2}]$  levels at 5676 and 7647 cm<sup>-1</sup>, respectively. It is reasonable to assign the  $a_1$  band (Fig. 4(c)) at 5678  $\pm$  24 cm<sup>-1</sup> (with respect to the EA defining band X<sub>1</sub>-1) to be the  $a^5\Sigma^- \leftarrow X^4\Sigma^- (0 \leftarrow 0)$  transition, and the strong and sharp  $b_1$  at  $7203 \pm 24 \text{ cm}^{-1}$  to be the  $b^1\Gamma \leftarrow X^4\Sigma^-$  (0  $\leftarrow$  0) transition. The weak  $\eta$  band in Fig. 4(c) can be assigned as the vibrationally hot band  $b^1\Gamma \leftarrow X^4\Sigma$  (0  $\leftarrow$  1). The  $b_1-\eta$  distance defines the vibrational frequency of the MoC<sup>-</sup> ground state to be  $928 \pm 8$  cm<sup>-1</sup>, which matches the MRCI value of 921 cm<sup>-1</sup> very well. The  $\varepsilon$  and  $\zeta$  bands observed at 600 nm excitation (Fig. 4(b)) may be assigned as  $b^{1}\Gamma \leftarrow a^{2}\Delta_{5/2}$  (0  $\leftarrow$  0) and  $b^{1}\Gamma \leftarrow a^{2}\Delta_{3/2} (0 \leftarrow 0)$ , respectively (Table II).

The MRCI calculations<sup>25</sup> predicted that the  $c^1\Delta[(3\sigma)^1$  $(1\delta)^1$ ] level of MoC is at 8198 cm<sup>-1</sup>, so the sharp c band at 8106 ± 24 cm<sup>-1</sup> (Fig. 4(c)) is assigned to  $c^1\Delta_2 \leftarrow X^4\Sigma^ (0 \leftarrow 0)$ . It is noteworthy that the optical spectroscopy<sup>22</sup> observed a  $\Omega = 2$  level (assigned as  ${}^{1}\Delta_{2}$  state) with the term value of 7834 cm<sup>-1</sup> (0.971 eV) while no band with the binding energy around  $2.331 \pm 0.10 \text{ eV} (1.360 + 0.971 \text{ eV})$  was observed at 500 nm excitation (Fig. 4(c)). It is noteworthy that the peak c  $(2.365 \pm 0.003 \text{ eV}, \text{ Table II})$  observed at 500 nm becomes very weak at 425 nm excitation and this peak is almost overlapped with a weak  $b_2$  peak (2.372 ± 0.003 eV) in Fig. 4(d). The  $b_2$  and  $b_1$  peaks have similar  $\beta$  parameters and the former can be assigned as  $b^1\Gamma \leftarrow a^2\Delta_{3/2}$   $(1 \leftarrow 0)$ as shown in Table II. Based on the MRCI calculations,<sup>25</sup> the d and e bands (Fig. 4(d)) can be tentatively assigned as the  ${}^{5}\Pi[(3\sigma)^{1}(1\delta)^{2}(1\pi)^{1}] \leftarrow X^{4}\Sigma^{-}$  and  ${}^{1}\Sigma[(1\delta)^{2}] \leftarrow X^{4}\Sigma^{-}$ transitions, respectively.

#### **B.** Computational results

The computational results of this study are listed in Table III, in which available experimental results<sup>21,27</sup> are also given for a comparison. The experimental bond lengths of NbN ( $X^{3}\Delta$ ) and MoC ( $X^{3}\Sigma^{-}$ ) can be well reproduced (within ±2 pm) by the CCSD(T) calculations. The calculations correctly

TABLE III. Comparison between theory and experiment for the bond lengths  $(r_e)$  and relative energies  $(T_e)$  of NbN<sup>-</sup>, MoC<sup>-</sup>, and their neutral species.

	r <sub>e</sub> (pm)		$T_{\rm e}({\rm eV})$		
	Theory	Experiment	Theory	Experiment	
$\overline{\text{NbN}^{-}(X^{2}\Delta_{3/2})}$	167.0		0	0	
NbN <sup>-</sup> ( $X^2\Delta_{5/2}$ )			0.107	0.111	
NbN <sup>-</sup> ( $a^4\Sigma^-$ )	169.0		0.762		
NbN( $X^{3}\Delta$ )	165.0	166.2 <sup>a</sup>	1.487	1.450	
$MoC^{-}(X^{4}\Sigma^{-})$	170.0		0	0	
$MoC^{-}(a^2\Delta_{3/2})$	170.5		0.190	0.273	
$MoC^{-}(a^2\Delta_{5/2})$			0.322	0.420	
$\frac{MoC(X^{3}\Sigma^{-})}{}$	166.0	167.6 <sup>b</sup>	1.382	1.360	

<sup>a</sup>Reference 27. <sup>b</sup>Reference 21.

predicted that the bond length of MoC ( $X^{3}\Sigma^{-}$ ) is slightly longer than that of NbN ( $X^{3}\Delta$ ). The EA values of NbN and MoC molecules are also very well reproducible, within ±0.04 eV for the absolute values and  $\pm 3.2\%$  for the relative values. In addition, the calculations correctly predicted that the EA of NbN  $(1.450 \pm 0.003 \text{ eV})$  is slightly larger than that of MoC  $(1.360 \pm 0.003 \text{ eV})$ . The term values of the SO components of the  $a^2 \Delta_{3/2}$  and  $a^2 \Delta_{5/2}$  for MoC<sup>-</sup> are calculated to be 0.190 and 0.322 eV, respectively. These two values are lower than the corresponding experimental data (0.273 and 0.420 eV) by less than 0.1 eV. As a result, the quantum chemistry calculations are in good support of the related assignments made in this study, particularly for the assignments of the  $\beta$  and the  $\delta$  bands of MoC<sup>-</sup> (Fig. 4). Note that the  $\beta$  and the  $\delta$  bands provide new information to determine the energies of the first EESs of both MoC<sup>-</sup> and MoC.

## **IV. DISCUSSION**

As summarized in Fig. 5, the complex band systems of NbN (Fig. 3) and MoC (Fig. 4) are mainly due to many possible fillings of two electrons into three valence MOs: one  $\sigma$ -type



FIG. 5. Three molecular orbitals (a), filled with two electrons to generate different electron configurations and energy levels for NbN (b), and MoC (c). The energy levels of MoC are taken from this work and those of NbN are taken from Refs. 28 and 31. The energies are in unit of  $cm^{-1}$ .

MO (3 $\sigma$ ) characterized with the metal 5s AO and two  $\delta$ -type MOs (1 $\delta$ ) that are essentially the metal  $4d_{xy}$  and  $4d_{x2-y2}$  AOs (Fig. 5(a)). The three possible electron configurations  $(3\sigma)^1(1\delta)^1$ ,  $(1\delta)^2$ , and  $(3\sigma)^2$  can result in nine energy levels including the  $\Omega$  splittings. Six of the nine levels of NbN [except  ${}^{3}\Delta_{3}$ ,  ${}^{3}\Sigma_{0}^{-}$ , and  ${}^{1}\Sigma_{0}^{+}/(1\delta)^{2}$ ] and eight of the nine levels of MoC [except  ${}^{1}\Sigma_{0}^{+}/(3\sigma)^{2}$ ] have been touched by the PEI spectroscopy in this study (Tables I and II).

The  $(3\sigma)^1(1\delta)^1$  electronic configuration results in ground electronic state of NbN and the first EES of MoC. The  ${}^3\Delta_3 - {}^3\Delta_2$ and  ${}^3\Delta_2 - {}^3\Delta_1$  splittings of NbN (491 and 400 cm<sup>-1</sup>) are smaller (by about 100 cm<sup>-1</sup>) than the corresponding values of the MoC system (604 and 492 cm<sup>-1</sup>). This is reasonable since the heavier metal atoms have larger atomic SO parameters.<sup>50</sup> The distances between the  ${}^1\Delta_2$  and the  ${}^3\Delta_2$  levels (5797 and 4065 cm<sup>-1</sup>) are similar in both the NbN and MoC systems. The  ${}^3\Delta_{1,2} \leftarrow {}^2\Delta_{3/2}$  (0, 1  $\leftarrow$  0) transitions result in similar spectral pattern of the four X bands of NbN<sup>-</sup> (Fig. 3(a)) versus that of the four  $\delta$  bands of MoC<sup>-</sup> (Fig. 4(c)). Both of the band systems have large and positive  $\beta$  parameters (1.9–2.0 for NbN<sup>-</sup> and 1.4–1.7 for MoC<sup>-</sup>, see Tables I and II).

The  $(1\delta)^2$  electronic configuration results in the ground electronic state of MoC and the EESs of NbN. The  ${}^3\Sigma_1 {}^{-3}\Sigma_0 {}^{-3}\Sigma_0$ splitting of MoC determined in this work is 161 cm<sup>-1</sup> which is in agreement with the estimation (155 cm<sup>-1</sup>) by the second order SO effect.<sup>21</sup> However, an anomalously large  ${}^3\Sigma_1 {}^{-3}\Sigma_0 {}^{-3}$ splitting of 492 cm<sup>-1</sup> was reported for NbN. This large splitting is due to the fact that there is accident configuration interaction between the  ${}^3\Sigma_0 {}^{-}(1\delta)^2$  level and the  ${}^1\Sigma_0 {}^{+}(3\sigma)^2$ level, the latter of which is just above the  ${}^3\Sigma_1 {}^{-1}$  level by 260 cm<sup>-1</sup>.<sup>31</sup> The  ${}^1\Sigma_0 {}^{+}(3\sigma)^2$  level of MoC is high in energy<sup>25</sup> and the corresponding accident interaction is negligible, so the  ${}^3\Sigma_1 {}^{-3}\Sigma_0 {}^{-1}$  splitting (161 cm<sup>-1</sup>) can be well predicted (155 cm<sup>-1</sup>).<sup>21</sup> It is noteworthy that the distances between the  ${}^1\Sigma_0 {}^{+}(1\delta)^2$  levels and the  ${}^3\Sigma_0 {}^{-}(1\delta)^2$  levels are similar (8796 versus 9897 cm<sup>-1</sup>) for both NbN and MoC systems.

The above analysis indicates that the detailed electronic structures for each of the  $(3\sigma)^1(1\delta)^1$  and  $(1\delta)^2$  configurations can be similar for the NbN and MoC iso-electronic systems. However, it turns out that the relative energy of the  $1\delta$  MO versus the  $3\sigma$  MO is significantly lower in MoC than that in NbN, which favors the  $(1\delta)^2$  and  $(3\sigma)^1(1\delta)^1$  ground state configurations for MoC and NbN, respectively. Moreover, the  ${}^{1}\Sigma_{0}{}^{+}(3\sigma)^{2}$  level of NbN is located at 5863 cm<sup>-1</sup>. In contrast, the  ${}^{1}\Sigma_{0}^{+}(3\sigma)^{2}$  level of MoC should be very high in energy as it was not predictable by the MRCI calculations on the low-lying singlet electronic states covering more than 20 000 cm<sup>-1</sup>.<sup>25</sup> It is known that the heavier 4d metal atoms have apparently increased stability of the 4d orbitals.<sup>21,32</sup> In contrast, the stability of the 5s orbital does not change much along the 4d metal series, so the MoC favors more 4d population than NbN  $[(1\delta)^2$  versus  $(3\sigma)^1(1\delta)^1$  for the ground states]. In line with the above fact, the ZrO molecule which is also an iso-electronic system of MoC has the  ${}^{1}\Sigma_{0}^{+}(3\sigma)^{2}$  ground state.<sup>51</sup>

When three electrons fill the three MOs (Fig. 5(a)) to form the NbN<sup>-</sup> and MoC<sup>-</sup> anions, the less favorable 4d population of the former over the latter results in the  ${}^{2}\Delta[(1\delta)^{1}(3\sigma)^{2}]$  and  ${}^{4}\Sigma^{-}[(1\delta)^{2}(3\sigma)^{1}]$  ground states, respectively. The  ${}^{4}\Sigma^{-}[(1\delta)^{2}(3\sigma)^{1}]$  state of NbN<sup>-</sup> is above the ground state by

0.762 eV as predicted by the CCSD(T) calculations (Table III). Such a high energy level was not populated in the experiment as can be seen from the fact that the PEI spectra of NbN<sup>-</sup> (Fig. 3) is rather clean (most transitions are cold bands) and the assignments (Table I) is straightforward. In contrast, the  $^{2}\Delta_{3/2}[(1\delta)^{1}(3\sigma)^{2}]$  state of MoC<sup>-</sup> is above the ground state by only 0.273 eV (2202 cm<sup>-1</sup>), so the assignments of the MoC<sup>-</sup> spectra (Fig. 4) suffered from presence of many electronically hot bands even in the EA defining region. In addition to the  $^{2}\Delta_{3/2}$  and  $^{2}\Delta_{5/2}$  levels of MoC<sup>-</sup> (Table III), a few other lowlying EESs of the anion were populated in the experiment and could be responsible for the unassigned  $\alpha$  and  $\gamma$  bands listed in Table II. Further high-level quantum chemistry calculations as performed for the neutral MoC<sup>25</sup> is requested for the anionic MoC<sup>-</sup> system.

Fig. 4 indicates that for MoC<sup>-</sup>, the X<sub>1</sub> and X<sub>2</sub> bands are in between  $\beta/\gamma$  and  $\delta_{1-4}$  hot bands. The observation of the three  $\Omega$  components (Fig. 4(b)-inset) confirms the assignment of  ${}^{3}\Sigma^{-}[(1\delta)^{2}] \leftarrow {}^{4}\Sigma^{-}[(1\delta)^{2}(3\sigma)^{1}]$  to the X<sub>1</sub> band. The determination of the small  $\Omega$  splittings of the  ${}^{3}\Sigma_{0,1}^{-}$  $(161 \pm 16 \text{ cm}^{-1})$  and  ${}^{4}\Sigma_{1/2,3/2}^{-}$  levels ( $80 \pm 16 \text{ cm}^{-1}$ ) was benefited from the improved absolute energy resolution of the PEIS over the traditional PES.<sup>18–20</sup> The high-resolution availability of the PEIS has been used to investigate the complex vibrational structures of polyatomic molecules and cluster species.<sup>4,52–54</sup> This study demonstrates that the complex electronic structures resulted from electron fillings into nearly degenerated metal valence orbitals can be better resolved by the imaging technique.

# **V. CONCLUSION**

Photoelectron imaging spectroscopy of two iso-electronic molecules NbN<sup>-</sup> and MoC<sup>-</sup> has been studied. For the NbN system, six electronic levels  $X^{3}\Delta_{1}$ ,  $X^{3}\Delta_{2}$ ,  $a^{1}\Delta_{2}$ ,  $A^{3}\Sigma_{1}^{-}$ ,  $b^{1}\Sigma_{0}^{+}$ , and  $c^{1}\Gamma_{4}$  have been reached by the imaging spectroscopy and the assignments were very well supported by literature reported optical spectroscopy. For the MoC system, more than eight electronic levels  $X^{3}\Sigma_{0}^{+}$ ,  $X^{3}\Sigma_{1}^{+}$ ,  $A^{3}\Delta_{1}$ ,  $A^{3}\Delta_{2}$ ,  $A^{3}\Delta_{3}$ ,  $a^{5}\Sigma^{-}$ ,  $b^{1}\Gamma_{4}$ ,  $c^{1}\Delta_{2}$ , and possibly  $d^{5}\Pi$  and  $e^{1}\Sigma_{0}^{+}$  have been visited. The increased stability of the 4d orbital of Mo versus Nb causes rather different electronic structures between MoC and NbN systems. The MoC<sup>-</sup> imaging spectra were much more complex than the NbN<sup>-</sup> spectra because several low-lying electronic states of MoC<sup>-</sup> resulted in additional hot bands. The simpler NbN<sup>-</sup> spectra were helpful in the assignments of the more complex MoC<sup>-</sup> spectra. The electron affinities of NbN and MoC have been determined to be  $1.450 \pm 0.003$  eV and  $1.360 \pm 0.003$  eV, respectively. The first electronically excited state of MoC<sup>-</sup>, the  $a^2\Delta_{3/2}$  level, is above the ground state  $X^4 \Sigma_{1/2}^{-}$  by 0.273  $\pm$  0.003 eV (2202  $\pm$  24 cm<sup>-1</sup>). The spin-orbit splitting of the NbN<sup>-</sup>  $X^2\Delta_{5/2}/X^2\Delta_{3/2}$  is 0.111  $\pm$  0.001 eV (895  $\pm$  8 cm<sup>-1</sup>) and the splitting of the MoC<sup>-</sup>  $a^2 \Delta_{5/2}/a^2 \Delta_{3/2}$  is 0.147 ± 0.010 eV (1186 ± 80 cm<sup>-1</sup>). The vibrational frequencies of the ground electronic states of NbNand MoC<sup>-</sup> are  $944 \pm 16$  cm<sup>-1</sup> and  $928 \pm 8$  cm<sup>-1</sup>, respectively. The good energy resolution of the imaging spectroscopy resolved the small  $\Omega$  spittings of 80 ± 16 cm<sup>-1</sup> for the X<sup>4</sup> $\Sigma$ <sup>-</sup> state of MoC<sup>-</sup> and 161 ± 16 cm<sup>-1</sup> for the  $X^{3}\Sigma^{-}$  state of MoC.

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- <sup>1</sup>Z. Luo, H. Huang, Z. Zhang, Y.-C. Chang, and C. Y. Ng, J. Chem. Phys. **141**, 024304 (2014).
- <sup>2</sup>S.-B. Cheng and A. W. Castleman, Jr., J. Phys. Chem. A **118**, 6935 (2014).
- <sup>3</sup>Z.-Y. Li, Z. Yuan, Y.-X. Zhao, and S.-G. He, Chem. Eur. J. 20, 4163 (2014).
- <sup>4</sup>I. León, Z. Yang, and L.-S. Wang, J. Chem. Phys. 140, 084303 (2014).
- <sup>5</sup>B. R. Visser, M. A. Addicoat, J. R. Gascooke, W. D. Lawrance, and G. F. Metha, J. Chem. Phys. **138**, 174310 (2013).
- <sup>6</sup>M. Kavitha, G. Sudha Priyanga, R. Rajeswarapalanichamy, and K. Iyakutti, J. Phys. Chem. Solids **77**, 38 (2015).
- <sup>7</sup>J. Yang, R. H. Judge, and D. J. Clouthier, J. Chem. Phys. **135**, 124302 (2011).
- <sup>8</sup>F. Wang and T. C. Steimle, J. Chem. Phys. **136**, 044312 (2012).
- <sup>9</sup>O. Krechkivska and M. D. Morse, J. Phys. Chem. A **117**, 13284 (2013).
- <sup>10</sup>H.-T. Liu, D.-L. Huang, Y. Liu, L.-F. Cheung, P. D. Dau, C.-G. Ning, and L.-S. Wang, J. Phys. Chem. Lett. **6**, 637 (2015).
- <sup>11</sup>L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, and Y. Xu, Catal. Lett. **21**, 35 (1993).
- <sup>12</sup>D. Ma, Y. Shu, M. Cheng, Y. Xu, and X. Bao, J. Catal. **194**, 105 (2000).
- <sup>13</sup>F. Solymosi and R. Németh, Catal. Lett. **62**, 197 (1999).
- <sup>14</sup>F. Solymosi, R. Németh, L. Óvári, and L. Egri, J. Catal. 195, 316 (2000).
- <sup>15</sup>D.-V. N. Vo and A. A. Adesina, Appl. Catal., A **399**, 221 (2011).
- <sup>16</sup>W. F. Chen, C. H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu, and R. R. Adzic, Energy Environ. Sci. 6, 943 (2013).
- <sup>17</sup>J. Gao, Y. Zheng, G. B. Fitzgerald, J. de Joannis, Y. Tang, I. E. Wachs, and S. G. Podkolzin, J. Phys. Chem. C 118, 4670 (2014).
- <sup>18</sup>D. M. Neumark, J. Phys. Chem. A **112**, 13287 (2008).
- <sup>19</sup>I. León, Z. Yang, H.-T. Liu, and L.-S. Wang, Rev. Sci. Instrum. 85, 083106 (2014).
- <sup>20</sup>X. Li, S. S. Liu, W. Chen, and L.-S. Wang, J. Chem. Phys. **111**, 2464 (1999).
- <sup>21</sup>D. J. Brugh, T. J. Ronningen, and M. D. Morse, J. Chem. Phys. **109**, 7851 (1998).
- <sup>22</sup>R. S. DaBell, R. G. Meyer, and M. D. Morse, J. Chem. Phys. **114**, 2938 (2001).
- <sup>23</sup>H. Wang, W. L. Virgo, J. Chen, and T. C. Steimle, J. Chem. Phys. **127**, 124302 (2007).
- <sup>24</sup>I. Shim and K. A. Gingerich, J. Chem. Phys. 106, 8093 (1997).
- <sup>25</sup>P. A. Denis and K. Balasubramanian, J. Chem. Phys. **125**, 024306 (2006).
- <sup>26</sup>C. Berkdemir, S.-B. Cheng, and A. W. Castleman, Jr., Int. J. Mass Spectrom. 365–366, 222 (2014).
- <sup>27</sup>T. M. Dunn and K. M. Rao, Nature 222, 266 (1969).
- <sup>28</sup>R. S. Ram and P. F. Bernath, J. Mol. Spectrosc. **201**, 267 (2000).
- <sup>29</sup>R. S. Ram and P. F. Bernath, J. Mol. Spectrosc. 243, 62 (2007).
- <sup>30</sup>Y. Azuma, J. A. Barry, M. P. J. Lyne, A. J. Merer, J. O. Schröder, and J. L. Féménias, J. Chem. Phys. **91**, 1 (1989).
- <sup>31</sup>Y. Azuma, G. Huang, M. P. J. Lyne, A. J. Merer, and V. I. Srdanov, J. Chem. Phys. **100**, 4138 (1994).
- <sup>32</sup>S. R. Langhoff and C. W. Bauschlicher, J. Mol. Spectrosc. **143**, 169 (1990).

- <sup>33</sup>A. Sanov, Annu. Rev. Phys. Chem. **65**, 341 (2014).
- <sup>34</sup>B. Xu, J.-H. Meng, and S.-G. He, J. Phys. Chem. C **118**, 18488 (2014).
- <sup>35</sup>B. Xu, Y.-X. Zhao, X.-L. Ding, Q.-Y. Liu, and S.-G. He, J. Phys. Chem. A 117, 2961 (2013).
- <sup>36</sup>D. C. Morton, Astron. Astrophys., Suppl. Ser. 77, 119 (1991).
- <sup>37</sup>X. Wu, Z. Qin, H. Xie, R. Cong, X. Wu, Z. Tang, and H. Fan, J. Phys. Chem. A **114**, 12839 (2010).
- <sup>38</sup>V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, Rev. Sci. Instrum. **73**, 2634 (2002).
- <sup>39</sup>D. Dill, J. Chem. Phys. 65, 1130 (1976).
- <sup>40</sup>C. M. Oana and A. I. Krylov, J. Chem. Phys. **131**, 124114 (2009).
- <sup>41</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Cioslowski, and D. J. Fox, GAUSSIAN 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.
- <sup>42</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
- <sup>43</sup>J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
- <sup>44</sup>K. A. Peterson, D. Figgen, M. Dolg, and H. Stoll, J. Chem. Phys. **126**, 124101 (2007).
- <sup>45</sup>T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
- <sup>46</sup>H. J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988).
- <sup>47</sup>H. -J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, P. Celani, G. Knizia, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, MOLPRO, version 2010.1, a package of *ab initio* programs, 2010, see http://www.molpro.net.
- <sup>48</sup>A. Berning, M. Schweizer, H.-J. Werner, P. J. Knowles, and P. Palmieri, Mol. Phys. **98**, 1823 (2000).
- <sup>49</sup>K.-i. C. Namiki and T. C. Steimle, J. Chem. Phys. **111**, 6385 (1999).
- <sup>50</sup>M. Vijayakumar and M. S. Gopinathan, J. Mol. Struct.: THEOCHEM 361, 15 (1996).
- <sup>51</sup>S. J. Peppernick, K. D. D. Gunaratne, and A. W. Castleman, Jr., Proc. Natl. Acad. Sci. U. S. A. **107**, 975 (2010).
- <sup>52</sup>J. B. Kim, M. L. Weichman, and D. M. Neumark, J. Am. Chem. Soc. **136**, 7159 (2014).
- <sup>53</sup>H.-T. Liu, C.-G. Ning, D.-L. Huang, P. D. Dau, and L.-S. Wang, Angew. Chem., Int. Ed. **52**, 8976 (2013).
- <sup>54</sup>H.-T. Liu, C.-G. Ning, D.-L. Huang, and L.-S. Wang, Angew. Chem., Int. Ed. 53, 2464 (2014).