A Velocity Map Imaging Study of Multiphoton Photodissociation and Photoionization Dynamics in Niobium Oxide, NbO

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Dedication

This article is submitted to the Festschrift edition of Molecular Physics in honour of Prof Dave Parker, towering figure in chemical physics and one of the founders of the velocity map imaging technique employed here.

ABSTRACT

Velocity map imaging has transformed our capabilities in terms of determining photofragmentation and photoionization thresholds. Here, we present an investigation into the multi-photon dissociation and photoionization dynamics of niobium monoxide (NbO) probed using velocity-map imaging via the $C^4\Sigma^- \leftarrow X^4\Sigma^-$ and $B^4\Pi \leftarrow X^4\Sigma^-$ transitions. Analysis of the kinetic energy release spectra permits determination of refined values of the dissociation energies for NbO and NbO⁺ of $60650 \pm 124 \text{ cm}^{-1}$ and $57414 \pm 124 \text{ cm}^{-1}$, respectively, in good agreement with previous values using other methods. With the same instrument, we have further recorded photoelectron images which exhibit a long progression assigned to production of ground state, $X^3\Sigma^- \text{ NbO}^+(v^+)$, for which a vibrational constant of $1002 \pm 11 \text{ cm}^{-1}$ is determined.

I. Introduction

The partially-filled *d*-orbitals in transition metal atoms give rise to a rich electronic structure in the simple molecules they form.[1] The fragmentation dynamics of transition metal chalcogenides reflect this complexity with many potential energy surfaces involved leading to a large number of possible reaction trajectories. Precise measurement of bond dissociation energies provides key information on the nature of the bonding involved as well as providing a test for accurate quantum chemical calculations.[2,3] Further afield, improved understanding of transition metal oxides is important to the astrochemistry community as these species are often identified in the spectra of stars. For example, VO is found in exoplanets atmospheres [4,5] and the subject of this study, niobium oxide (NbO) has been tentatively identified in the S-type star R. Cygni. [6]

The target of this study, NbO, has received considerable high-resolution spectroscopic attention in the visible region. [7-12] It was further the subject of a combined photoelectron spectroscopy and quantum chemical study by Dyke *et al.*[13] and it continues to attract considerable theoretical attention both in its own right and for its role in catalytic chemistry.[14]

One objective of this work is the direct determination of the bond dissociation energy of NbO. Traditionally this value is deduced from equilibrium constants for atomic and molecular species above condensed-phase samples superheated in a Knudsen cell.[5,15] These methods are prone to large uncertainties arising from the need for thermodynamics extrapolation. It often proves easier to determine dissociation energies of charged species using techniques such as guided ion beam mass spectrometry and these results can be combined with ionization energies (or electron affinities in the case of anions) via thermochemical cycles to determine neutral molecule bond energies. For example, the respective dissociation energies $D_0(\text{NbO})$ and $D_0(\text{NbO}^+)$ are linked by the respective ionization energies, E_i , of Nb and NbO:

$$D_0(\text{NbO}^+) + E_i(\text{NbO}) = D_0(\text{NbO}) + E_i(\text{Nb}). \quad (1)$$

The ionization energies can typically be measured with high precision, and hence a precise measurement of one dissociation energy is required to determine the other. For NbO, E_i has been measured to be 7.160 ± 0.004 eV by Looock *et al.* [16] using mass analysed threshold ionization and the ionization potential of the atom is known precisely at 6.75885 ± 0.00004 eV [17]. Guided ion beam collision induced dissociation measured $D_0(\text{NbO}^+) = 7.13 \pm 0.11$ eV [18] from which the neutral dissociation energy, $D_0(\text{NbO}) = 7.53 \pm 0.11$ eV can be fixed [16]. In this approach, necessarily, the precision of the result is always limited to that of the least well-determined value of the thermodynamic cycle.

Velocity map imaging (VMI), in principle provides a rather more direct measurement of dissociation energies by determining the total kinetic energy release in a photofragmentation process at known energy. In practice, though, metal atom-containing molecules, by virtue of their typical production (sputtering, high temperature ovens or laser ablation) are rarely produced cleanly and multiple measurements at different photolysis energies are typically required even to confirm the identity of the co-fragment. Where this can be done, however, extrapolation to zero kinetic energy release provides an accurate and precise measure of the dissociation threshold and we have recently used this technique to determine improved bond dissociation energies of a range of species, including CuO and Cu₂, [19] AgO and M-RG (M=Au, Ag; RG=Ar, Kr, Xe), [20] Au₂, [21] MoO and CrO [22] and, most recently, VO [23]. In several cases the revised values obtained from VMI have subsequently been confirmed by recent resonant multiphoton threshold onset spectroscopy of the form perfected by Morse and coworkers which relies on high density of states at dissociation thresholds (see, for example, ref [3]) .

Here, we extend our VMI investigations into *d*-block metal oxides with a multiphoton dissociation study of NbO excited *via* the $B^4\Pi$ and $C^4\Sigma^-$ states. The myriad low-lying electronic states of Nb leads to complex dissociation dynamics but extrapolation of the observed total photofragment kinetic energy release observed as a function of total photoexcitation energy in several channels yields an improved dissociation energies for both NbO and NbO⁺. The internal energy of the parent NbO, E_{NbO} , and photofragments, E_{Nb} and E_O , are related to the energy of n photons, $nh\nu$, the dissociation energy, $D_0(\text{NbO})$, and the total-kinetic energy release of both neutral fragments, $TKER$, as,

$$E_{NbO} + nh\nu = D_0(\text{NbO}) + E_{Nb} + E_O + TKER. \quad (2)$$

The internal energy of NbO prepared in a molecular beam is negligible. With knowledge of the photon energy and product state energies, the dissociation energy is determined by measuring the fragment kinetic energy for dissociation at different photon energies across the visible spectrum. This, in turn, is achieved using VMI following ionization of the Nb photofragment.

In a first for our Oxford metal cluster VMI instrument, we further demonstrate photoelectron imaging capability in a multiphoton ionization study of NbO *via* the $C^4\Sigma^-(v' = 1)$ state. Photoelectron images are assigned to discrete vibrational levels of the $X^3\Sigma^-$ and $^3\Delta$ states of NbO⁺. Production of the $^3\Sigma^-$ state leads to a long progression from which the vibrational constant is determined.

II. Experimental

The VMI instrument used in these studies is the same as that described in our recent photodissociation study of VO[23]. In brief, laser ablation of a rotating disc of pure niobium (Sigma Aldrich, 99.8%) using a nanosecond pulsed 532 nm laser generates Nb and NbO containing species which are entrained in a pulse of helium delivered *via* a solenoid valve (Parker-Hannifin, Series 9) from a stagnation pressure of 3 bar. Photoexcitation of NbO in visible part of the spectrum was provided by the focussed output of a pulsed optical parametric oscillator (OPO, Continuum Panther) or a dye laser (Sirah Cobra Sketch). The photoexcitation pulse results in both ionization and dissociation of NbO. Nb* photofragments are themselves photoionized within a VMI lens assembly with the same pulse. Ion extraction occurs collinear with the molecular beam and images are recorded at a 10 Hz using a commercial MCP/scintillator (P45)/camera assembly (Photek) employing on-the-fly centroid averaging. Reconstruction of the central slice of the ion sphere was performed using the pBASEX algorithm [24].

In the spectral region probed here (410 – 475 nm), the only two species detected in the mass spectrum were Nb⁺ and NbO⁺ suggesting the neutral beam comprises predominantly Nb atoms and NbO neutral. All VMI images presented here are either of Nb fragments or photoelectrons arising following excitation via the $C\ ^4\Sigma^-(\nu)$ or $B\ ^4\Pi$ states of NbO. A magnification factor of 1.055 is used throughout this work, consistent both with simulations of ion trajectories with our electrode arrangement and our previous experiments [22,23].

III. Results and Discussion

A. (1+n) REMPI Spectrum of NbO

To confirm the presence of neutral NbO in the molecular beam, the (1+n) resonance enhanced multiphoton ionization (REMPI) spectrum of NbO was recorded in the vicinity of $C^4\Sigma^- - X^4\Sigma^- (\nu, 0)$ transitions in the range 21000-24500 cm^{-1} . [7] **Figure 1a** shows the yield of NbO^+ ions produced as a function of photoexcitation laser wavenumber. In this spectral region, at least three photons are required to reach the first ionization energy of NbO at 7.160 ± 0.004 eV (57749 ± 33 cm^{-1}). [16] By assigning the transitions observed in the (1+n) REMPI spectrum, the nature and spectral position of the intermediate state available for the multi-photon fragmentation of NbO can be identified.

The NbO $X^4\Sigma^-$ ground state has been described by Brom *et al.* [15] and the molecular orbital picture is shown in **Figure 2(a)**. The three unpaired electrons occupy the non-bonding 2δ and 12σ orbitals formed from the Nb $4d$ and $5s$ atomic orbitals. The spectrum of niobium oxide (then known as columbium oxide, CbO) was first studied by Rao [12], who observed bands in the visible part of the spectrum later attributed to the $C^4\Sigma^- - X^4\Sigma^-$ [7-9,16,25] and $B^4\Pi - X^4\Sigma^-$ [8,10,11] transitions. The energies of the quartet states accessible in the visible region of the spectrum are summarized in **Figure 2(b)**. Both the X and C states are best describe by Hund's case (a) coupling [11]. This is somewhat unusual for $^4\Sigma$ states which are typically better described by case (b) [26]. However, the assignment is consistent with the large second order spin-orbit splittings of 62 cm^{-1} (X -state) and 60 cm^{-1} (C -state) [11], which Cheval *et al.* [7] attribute to interaction of the $^4\Sigma^-$ state with a $^2\Sigma^+$ state predicted *ca.* 10,000 cm^{-1} above the ground state.

Figures 1 (b) and (c) show simulations of the $C^4\Sigma^- - X^4\Sigma^-$ and $B^4\Pi - X^4\Sigma^-$ transitions using the PGOPHER software suite [27] with spectroscopic values from Cheval *et al.* [7] and

Kingston *et al.* [10]. A rotational and vibrational temperature of 150 K is assumed and peaks are convoluted with the 6 cm⁻¹ linewidth of the OPO fragmentation laser.

The REMPI spectrum is dominated by transitions *via* the $C^4\Sigma^-$ state which has its origin band at 21346 cm⁻¹, [7] but excitation to excited vibrational levels $v' = 1, 2$, and 3, are the strongest observed. Each vibrational band is split into three $C^4\Sigma^-_{|\Sigma'|} \leftarrow X^4\Sigma^-_{|\Sigma''|}$ components for transitions between the different fine structure components of the C and X states. The strong central component of the observed triplet can be attributed to $\Delta\Sigma = 0$ transitions which are allowed in Hund's case (a). Weaker, case (a) forbidden, $\Delta\Sigma = \pm 1$ are also observed due to the uncoupling of the spin from the nuclear axis (into Hund's case (b)) for higher rotational states [8]. Inefficient vibrational cooling in the molecular beam also results in hot bands observed at 22040, 22850 and 22670 cm⁻¹ with other features attributed to $B^4\Pi(v) - X^4\Sigma^-$ transitions.

B. Nb⁺ Photofragment Imaging via NbO $C^4\Sigma^-$ (v')

From the $C^4\Sigma^-$ state at least a further two photons are required to reach the dissociation threshold around 7.5 eV:

The Nb* atom photofragment in reaction (3) requires three additional photons to be ionized – a necessary precursor for VMI. **Figure 3** shows velocity-map images of Nb⁺ photoproducts produced following excitation *via* the NbO $C^4\Sigma^-$ ($v'=1-3$) levels (**Figure 3(a)-(c)**). Symmetrized raw images are shown in at the left hand side and the pBASEX [24] reconstructed central slices are shown in the centre. In both cases, the photoexcitation laser has its $\underline{E}$ vector polarised in vertically. Nb⁺ fragment kinetic energy release spectra are shown on the right hand side.

The fragment kinetic energy spectra in **Figure 3** describe the kinetic energy distributions of the Nb atom photofragments. From these, the total kinetic energy release, $TKER$, can be derived as,

$$TKER = \left(1 + \frac{m_{Nb}}{m_O}\right) f KE_{Nb} \quad (4)$$

for substitution into equation (2). Clearly, for a fixed photoexcitation energy, the $TKER$ is unique for each Nb*/O* dissociation channel. **Figures 4 (a), (b)** summarize the electronic terms of fragment Nb and O atoms accessible in the three- or four-photon dissociation of NbO in this spectral region. **Figure 4(c)** illustrates the photofragmentation process illustrating the complexity of the photodissociation dynamics in this region. The potential energy curve of the NbO $X^4\Sigma^-$ ground state is shown alongside different potential dissociation channels. Three-photon dissociation can only produce Nb* in conjunction with ground-state oxygen atoms whilst the four-photon fragmentation, can produce Nb* + O¹D₂ channels.

In total, 44 different Nb electronic states can be accessed either in combination with O ³P_J or ¹D₂ spin-orbit levels. This yields 176 discrete exit channels, each of which could potentially be observed with varying branching ratios in the recorded velocity-map imaging data. Despite the large number of possible product state combinations, the velocity-map images in **Figure 3** show distinct sets of features. These features have not been fully assigned and it is likely that additional studies with higher kinetic energy resolution and/or state-selective Nb photoionization will be necessary to distinguish unambiguously the underlying product channels. However, enough channels can be assigned with high confidence and these have been used to determine the bond dissociation energy.

C. Determination of the $D_0(\text{NbO})$, bond dissociation energy

To determine the bond dissociation energy of NbO, velocity-map images of the Nb* photoproducts were recorded at 50 different photon energies in the vicinity of the $C^4\Sigma^-(v'=1, 2, 3) \leftarrow X^4\Sigma^-(v''=0)$ transitions. A representative selection of images recorded *via* the $C^4\Sigma^-(v'=1)$ level are given in Figure 5. Each shows a clear series of rings corresponding to dissociation into different channels (NbO/O atom fragment quantum states). Both the relative intensities of these rings, which reflects the fluctuating branching ratios, and the kinetic energy release in each channel, vary with the photoexcitation energy.

From equation (2) it is easily shown that for any given Nb* + O* dissociation channel, the kinetic energy of the Nb* fragment is proportional to the total excitation energy ($= nh\nu$, in which n is the total number of photons involved):

$$fKE_{Nb} = \frac{nh\nu}{\left(1 + \frac{m_{Nb}}{m_O}\right)} - C, \quad (5)$$

where C is a constant which depends on the dissociation threshold and any internal energy of the NbO molecule. Hence, the slope of any graph of fKE_{Nb} as a function of excitation wavenumber confirms not only the mass of the cofragment (in this case the O atom) but also the total number of photons, n , involved in the dissociation process.

As can be seen from Figure 5, several features in peaks in the kinetic energy release spectra are common to different images but move smoothly to larger kinetic energy release as the photon wavenumber increases (shown in the figure with black, blue, red and green dashed lines) reflecting fragmentation at a higher overall energy.

In total, 39 images were recorded in the region of the $C^4\Sigma^-(v'=1) \leftarrow X^4\Sigma^-(v''=0)$ transition and the kinetic energy release spectra were fit to sums of Gaussian functions in order to identify individual dissociation channels. Figure 6 shows the resulting features plotted as a function of

photon energy. The clear linearity of these plots confirms that each represents a different dissociation channel. Four series, labelled I - IV, are particularly distinct, and correspond to the main spectral features observed in [Figure 5](#). The slopes extracted from these series confirm the O-atom as the co-fragment and are best fit assuming dissociation occurs at the four-photon level, though the experimental uncertainties do not exclude the possibility of some three-photon processes.

The velocity-map image recorded at 22002 cm^{-1} ([Figure 5\(a\)](#)) does not appear to fit the same trend. This image is recorded resonant with the $C\ ^4\Sigma^- \leftarrow X\ ^4\Sigma^- (2,1)$ hot-band transition (see [Figure 1](#)) and hence the total energy involved includes an extra 981 cm^{-1} of internal energy of which 144 cm^{-1} appears as Nb fragment kinetic energy by virtue of conservation of momentum. Consequently, the fragment kinetic energy release features are shifted by this 144 cm^{-1} to higher kinetic energy as indicated by the horizontal arrows in [Figure 5\(a\)](#). Weaker features at lower kinetic energies can be attributed to ground state NbO molecules dissociated non-resonantly or via the $B\ ^4\Pi \leftarrow X\ ^4\Sigma^- (8,0)$ transition which overlaps with the C-state in this spectral region. Having confirmed the O-atom as the co-fragment, using conservation of momentum the fragment kinetic energy release spectra of [Figures 5, 6](#) can be recast as total kinetic energy release and, together with a sensible estimate of the dissociation energy (the $60734 \pm 887\text{ cm}^{-1}$ from Looock *et al.*[16]), dissociation channels observed can be determined. These, in turn, can then be used to revise the dissociation energy:

$$E_{int,tot} = nh\nu - (D_0(\text{NbO}) + E_{Nb} + E_O) \quad (6)$$

[Figure 7](#) shows a summary of all available VMI data, recorded *via* the $C^4\Sigma^-$ ($v'=1, 2, 3$) levels plotted as *TKER versus* four photon energy. From this we can confidently assign four dissociation channels, highlighted in colour in the Figure, as shown in Table 1 all of which

correlate with the O 1D state. By fixing the slopes for these fits to unity – consistent with the four-photon dissociation of NbO – we can extrapolate each of these lines to zero kinetic energy release and, with knowledge of the quantum state energies, determine independent values for $D_0(\text{NbO})$. These are also given in Table 1 and agree within mutual uncertainties. Combined, these permit a best determination of the NbO bond dissociation energy of $60650 \pm 124 \text{ cm}^{-1}$ ($7.52 \pm 0.015 \text{ eV}$). This agrees very well with the $7.53 \pm 0.11 \text{ eV}$ ($60730 \pm 890 \text{ cm}^{-1}$) value reported by Looock *et al.* [16] from their MATI determination of the NbO ionization potential coupled with the collisional dissociation energy of NbO^+ ($7.13 \pm 0.11 \text{ eV}$) from Armentrout and co-workers.[18] In a rather circular argument, coupled with the well-known ionization energies of NbO [16] and Nb [17], our revised BDE for NbO implies a dissociation energy of NbO^+ of $57414 \pm 124 \text{ cm}^{-1}$ ($7.119 \pm 0.015 \text{ eV}$) clearly in agreement with the Armentrout value.

D. Photoelectron imaging of NbO photoionization

We have recently modified our VMI instrument to permit photoelectron imaging and have calibrated it using the well-known (2+1)-REMPI ionization of vanadium atoms *via* the $f^4F_J \leftarrow a^4F_J$ transition (see supporting information).

Figure 8 shows a typical photoelectron velocity-map image of NbO recorded at a photon energy of 22152 cm^{-1} , resonant with the $\text{NbO } C^4\Sigma^-(v' = 1) \leftarrow X^4\Sigma^-(v'' = 0)$ transition. The symmetrized raw image is shown on the left, the reconstructed image central and the extracted electron kinetic energy distribution on the right. The photoelectron spectrum shows a series of 12 features below 9000 cm^{-1} . The highest kinetic energy feature matches well with three-photon ionization of a ground state NbO as indicated by the arrow in **Figure 8**. Looock *et al* reported the NbO ionization energy as 57749 cm^{-1} [16]. Hence, the main series features observed are assigned to vibrational levels of the ground $X^3\Sigma^-$ state of the NbO^+ ion. A second, shorter progression is apparent in the low electron kinetic energy range and this is assigned to

vibrational levels of the excited $^3\Delta$ state of NbO produced in four-photon ionization from the NbO ground state. The corresponding calculated threshold (5200 cm^{-1}) is also marked in Figure 8. These photoionization schemes are illustrated in Figure 9(a). The low-lying electronic states of NbO^+ have been characterised in a photoelectron study by Dyke *et al.* [13] who reported a vertical ionization energy of 10.34 eV (83398 cm^{-1}) to the $^3\Delta$ excited state which could be accessed in a four-photon ionization.

The long progression of vibrational levels assigned in Figure 8 permits a determination of the harmonic ω_e vibrational constant for the $X\ ^3\Sigma^-$ state which is shown in Figure 9(b). The centre of the peaks identified by Gaussian fits to the photoelectron spectrum in Figure 8 are fit as a function of vibrational quantum number in NbO^+ . The linearity of this fit illustrates quite how good the harmonic approximation is and a vibrational wavenumber of $\omega_e = 1002 \pm 11\text{ cm}^{-1}$ for the $\text{NbO}^+ X\ ^3\Sigma^-$ state is derived from the slope. This compares with calculated values of 1067 cm^{-1} from Dyke *et al.* at the Hartree–Fock–Slater level [13] and 1044 cm^{-1} by Zhou and Andrews from density functional theory.[28] We are not aware of any previous experimental determination of this value though Zhou and Andrews did observe a 1001.1 cm^{-1} band in their matrix isolation infrared study which they tentatively assigned to NbO^+ . [28]

It is perhaps surprising that such a long progression is observed in ionization above the NbO^+ ground state. After all the $X\ ^3\Sigma^-$ state is expected to have very similar bond length to the neutral NbO $X\ ^4\Sigma^-$ state ($1.683\text{ \AA}$ experimentally and $1.690\text{ \AA}$ at the CCSD(T) level of theory [14]). However, the C state via which these excitations have been made has significantly longer bond length at $1.76\text{ \AA}$ [14] and hence the Franck-Condon factors from the $v=1$ level clearly permit access to the $\text{NbO}^+ X\ ^3\Sigma^- (v^+ = 0-8)$ levels.

IV. Conclusions

The multi-photon fragmentation and ionization dynamics of NbO have been studied by velocity map imaging. Photofragment imaging data recorded via the NbO $C\ ^4\Sigma^-$ state is interpreted in terms of four-photon fragmentation and the branching ratio of observed Nb* and O* quantum states is found to be dependent on the vibrational level of the intermediate C -state.

Analysis of Nb⁺ fragment kinetic energy distributions at different photon energies permits confident assignment of four dissociation channels and yields a refined value of the NbO dissociation energy of $60650 \pm 124\text{ cm}^{-1}$. Coupled with the well-known ionization energies of ionization energies of Nb and NbO, $D_0(\text{NbO}^+)$ is determined as $57414 \pm 124\text{ cm}^{-1}$, in excellent agreement with a previously determined value of the NbO⁺ dissociation energy by Sievers *et al.* [18] using collision induced dissociation.

We also report the first photoelectron imaging data from our instrument. The observed photoelectron spectrum is assigned to a long progression of vibrational states of the ground $X\ ^3\Sigma^-$ state of the NbO⁺ ion along with a shorter progressions tentatively assigned to production of the excited $^3\Delta$ state. An analysis of the spacing of the observed vibrational levels yielded a harmonic vibrational constant of the $X\ ^3\Sigma^-$ state, $\omega_e = 1002 \pm 11\text{ cm}^{-1}$, which we believe to be the first secure experimental determination of this value.

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VI. References

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Table 1. Assignment of series A, B, C and D in Figure 7. The bond dissociation energy $D_0(\text{NbO})$ is determined by extrapolation to zero kinetic energy release for each respective dissociation channel.

Series	Product States	$E_{\text{Nb}^*} + E_{\text{O}^*}$ /cm ⁻¹	$D_0(\text{NbO})$ /cm ⁻¹
A	Nb($b^4D_{7/2}$) + O(1D_2)	15412 ± 65	60580 ± 150
	Nb($b^4D_{3/2}$) + O(1D_2)		
	Nb($b^4D_{1/2}$) + O(1D_2)		
	Nb($b^4D_{5/2}$) + O(1D_2)		
B	Nb($b^4P_{3/2}$) + O(1D_2)	14211 ± 30	60619 ± 189
C	Nb($a^2D_{5/2}$) + O(1D_2)	10181 ± 55	60627 ± 72
	Nb($a^2P_{1/2}$) + O(1D_2)		
D	Nb($a^4D_{7/2}$) + O(1D_2)	9422 ± 62	60773 ± 83
	Nb($a^2G_{9/2}$) + O(1D_2)		
	Nb($a^2D_{3/2}$) + O(1D_2)

Figure 1. (a) (1+2) REMPI spectrum of the NbO molecule in the vicinity of the $C^4\Sigma^- \leftarrow X^4\Sigma^-$ ($v', 0$) transition. The hot band transitions (2,1), (3,1) and (4,1) are also assigned. Other bands are attributed to resonant ionization via the B -state; (b) simulation of the $C^4\Sigma^- \leftarrow X^4\Sigma^-$ transition based on spectroscopic values in Reference [7]; red bands correspond to transitions which are forbidden in Hund's case (a); (c) simulation of the $B^4\Pi \leftarrow X^4\Sigma^-$ transition based on spectroscopic values in Reference [10].

Figure 2. (a) Electron configuration of the $X^4\Sigma^-$ ground state of NbO adapted from [15]. The three unpaired electrons occupy the non-bonding 2δ and 12σ orbitals. (b) Energies of the low-lying quartet electronic states [7,8] – six doublet states in the same energy range are also known.

Figure 3. Velocity map images of Nb^* fragments produced by photoexcitation via $C^4\Sigma^-$ ($v' = 1, 2, 3$). Symmetrized raw images are shown on the left, Abel-inverted images in the centre, and the Nb^* fragment kinetic energy (fKE_{Nb}) distributions on the right. fKE_{Nb} distributions are compared with open dissociation channels assuming three-photon (red ticks) and four-photon (blue ticks) fragmentation.

Figure 4. (a), (b) Accessible electronic states of Nb and O atoms following three and four-photon dissociation of NbO. (c) Potential energy curve of the $\text{NbO}(X^4\Sigma^-)$ ground state and energies of different Nb+O product state combinations; black, blue and red product states correspond to Nb^* produced in sextet, quartet and doublet states, respectively. Three-photon fragmentation can only access the O^3P_J ground state while O^1D_2 can be reached in four-photon fragmentation at these photon energies.

Figure 5. Nb^* velocity-map images and fragment kinetic energy distributions, fKE_{Nb} , recorded at different photon energies in the vicinity of the $C^4\Sigma^- \leftarrow X^4\Sigma^-(1,0)$ and $B^4\Pi \leftarrow X^4\Sigma^-(8,0)$ transitions. The product kinetic energy distributions are fitted with Gaussian functions to identify the discrete dissociation channels observed. Several channels are common to multiple images (see black, blue, red and green dashed lines). The 22002 cm^{-1} image in (a) is recorded resonant with the $C^4\Sigma^-(v'=2) \leftarrow X^4\Sigma^-(v''=1)$ hot-band transition and the additional quantum of ground state vibrational energy shifts the observed features by 144 cm^{-1} to higher kinetic energies as indicated.

Figure 6. Dissociation channels observed in 39 velocity-map images recorded in the region of the $C\ ^4\Sigma^- \leftarrow X\ ^4\Sigma^- (1,0)$ transition in NbO. The fits to series I-IV confirm four-photon dissociation of NbO. Photodissociation in the region. 22000-22025 cm^{-1} comprises transitions via the (2,1) hot-band and of the $B\ ^4\Pi \leftarrow X\ ^4\Sigma^- (8,0)$. The additional vibrational quantum of the ground state energy is reflected in the photofragment kinetic energy distributions (grey circles) and are excluded from the fits.

Figure 7. Observed dissociation channels plotted as total kinetic energy release as a function of total excitation wavenumber. Series A-D are assigned in Table 1 and used to determine $D_0(\text{NbO})$. Grey points indicate channels which have not been assigned unambiguously.

Figure 8. Photoelectron image recorded at a photon energy of 22152 cm^{-1} , resonant with the $\text{NbO } C^4\Sigma^-(v' = 1) \leftarrow X^4\Sigma^-(v'' = 0)$ transition. (a) symmetrized raw image; (b) reconstructed central slice; (c) Photoelectron kinetic energy distribution fit (green line) with individual Gaussian functions (red line); accessible ionization thresholds at the three and four photon levels are indicated.

Figure 9. (a) Schematic diagram of the electronic and vibrational states involved in the three-photon and four-photon ionization (see text for details), and (b) observed energies of the vibrational levels in the $X^3\Sigma^-$ state of NbO^+ . The slope enables determination of a vibrational constant of $\omega_e = 1002 \pm 11 \text{ cm}^{-1}$.