Photodissociation Dynamics and the Dissociation Energy of Vanadium Monoxide, VO, Investigated using Velocity Map Imaging

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Supporting Information

A. Identification of the dissociation co-fragment

For two-body photodissociation at the *n* photon level of the diatomic molecule VX conservation of energy requires:

$$E_{\mathrm{VX}} + nh\nu = D_0(\mathrm{V}-\mathrm{X}) + E_{\mathrm{V}} + E_{\mathrm{X}} + TKER \qquad (1)$$

where E_{VX}, E_{V}, and E_{X} are the internal energies of the parent VX molecule, the V atom photofragment, and the co-fragment, X, respectively. D_0(V-X) is the ground state dissociation energy of VX, and *TKER* is the total kinetic energy release. Conservation of momentum requires allows the *TKER* in Equation 1 to be expressed in terms of the V fragment *KER*

$$TKER = KER(\mathrm{V}) \times \left(1 + \frac{m_{\mathrm{V}}}{m_{\mathrm{X}}}\right). \qquad (2)$$

Substitution of Equation 2 into Equation 1, followed by re-arrangement, yields the following expression for *KER*(V):

$$KER(\mathrm{V}) = h\nu \times \left(\frac{n}{1+ m_{\mathrm{V}}/m_{\mathrm{X}}}\right) - \frac{k}{1+ m_{\mathrm{V}}/m_{\mathrm{X}}}. \qquad (3)$$

Hence a plot of *KER*(V) versus photon energy, $h\nu$, is a linear function with a slope of $n/(1+m_{\mathrm{V}}/m_{\mathrm{X}})$ allowing the number of photons involved in a photofragmentation process and the identity of the co–fragment X can be determined. A plot of all measured V atom *KER*s in the photon energy range 19912–20072 cm^{-1} is shown in Figure 1 (top). A linear fit to the measured *KER* values gives a slope of 0.716 ± 0.061.

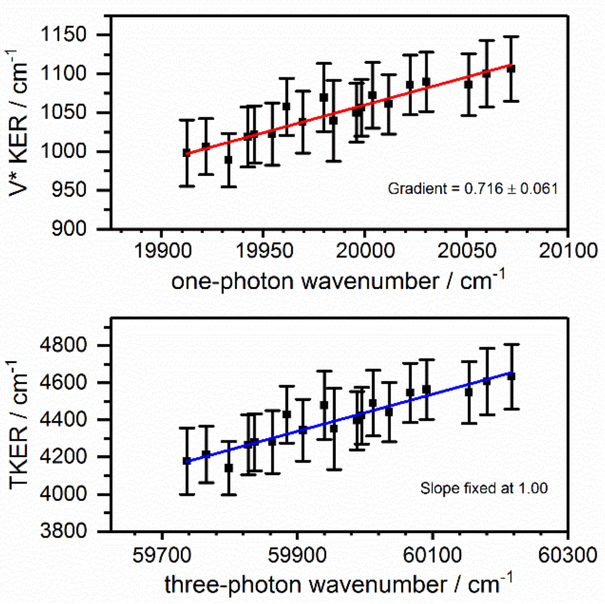

Figure S1. *Top:* Vanadium atom kinetic energy release (KER) as a function of one-photon energy between 19912-20072 cm^{-1}. A linear function fitted to the experimental data gives a gradient of 0.716 ± 0.061 sufficient to identify the co–fragment at an O–atom. *Bottom:* TKER plotted against three-photon wavenumber assuming V + O cofragments. The slope of the fitted linear function is fixed at 1, yielding an *x*–intercept of 55560 ± 170 cm^{-1}. The error bars in both datasets correspond to the Full-Width-Half-Maximum (FWHM) of each fitted Gaussian used to identify the centre of each peak.

Table S1 lists possible a range of plausible co–fragment candidates with the corresponding number of photons required to dissociate the parent molecule. Given that an integer number of photons must be involved, the most likely co-fragment is oxygen, justified further by the fact that VO is the only molecular species observed in the molecular beam.

Table S1. List of potential co-fragment candidates; *n* refers to the number of photons needed to dissociate the parent species. The oxygen co-fragment gives the required number of photons closest to an integer value. Errors in *n* arise from the uncertainty (standard deviation) in the gradient of the fitted-line using linear regression.

Slope	Co-fragment (X)	Number of photons (*n*)
0.716 ± 0.061	V	1.432 ± 0.122
	V_2	1.074 ± 0.092
	C	3.759 ± 0.321
	N	3.324 ± 0.284
	O	2.998 ± 0.256
	He	18.9751.622

B. Best determination of the VO dissociation energy

The V* *a* ^{2}G + O ^{3}P channel is confidently assigned in several images recoded *via* $C\ ^4\Sigma^-$ (v' = 5, 6, 7) allowing precise extrapolation to TKER = 0 under the assumption of dissociation the three-photon level. This, in turn, provides a best estimate of the VO experimental dissociation energy of 53126 ± 263 cm^{-1}.

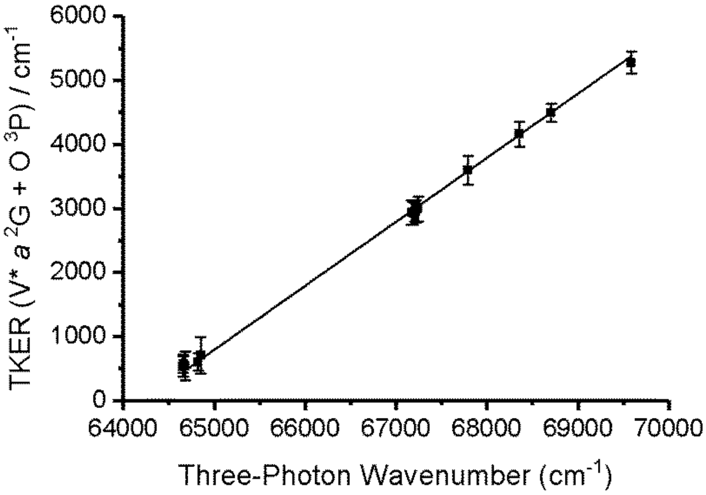

Figure S2: Extrapolation of the TKER in the V* *a* ^{2}G + O ^{3}P channel as a function of total excitation wavenumber. The excellent fit to a straight line with slope fixed at unity (R^2 = 0.998) allows extrapolation to an *x*-intercept of 64212 ± 18 cm^{-1}. Observation of the same channel in images across the region (including to low TKER) provides the best estimate of the VO dissociation energy (53126 ± 263 cm^{-1}) in this study.

C. Calculation of $D_0(VO^+)$ and Comparison to Literature Values

Table S2 compares the bond energy of VO^+ determined from this study with various previously-determined experimental and theoretical values. The value determined in this work was calculated via a thermodynamic cycle involving the most precise values for the ionisation energies of V and VO (termed *IE*(V) and *IE*(VO), respectively), and the D_0(VO) determined from the VMI work presented.

Table S2. Experimental and theoretical literature values of the ground state dissociation energy of VO^+, $D_0(VO^+)$.

Author	D_0	Method	Year
Aristov and Armentrout.[1]	131 ± 5 kcal mol^{-1} 45800 ± 2000 cm^{-1} (5.68 ± 0.22 eV)	Guided Ion Beam Mass Spectrometry	1984
Dyke *et al.*[2]	48200 ± 807 cm^{-1} (5.98 ± 0.10 eV)	High-Temperature Photoelectron Spectroscopy	1985
Arisov and Armentrout.[3]	48400 ± 2820 cm^{-1} (6.00 ± 0.35 eV)	Collision-Induced Dissociation	1986
Fisher *et al.* [4]	48400 ± 807 cm^{-1} (6.00 ± 0.10 eV)	Thermodynamic Cycle *via* *IE*(VO), *IE*(M), and D_0(VO)	1990
Clemmer *et al.*[5]	46900 ± 1370 cm^{-1} (5.81 ± 0.17 eV)	Guided Ion Beam Mass Spectrometry	1991
Carter and Goddard III.[6]	128.3 kcal mol^{-1} 44870 cm^{-1} (5.56 eV)	All-electron *ab initio* GVBCI-SCF	1988
Broclawik.[7]	D_e = 55000 cm^{-1} (D_e = 6.82 eV)	LCGTO Spin-Polarised DFT	1995
Kretzschmar *et al.*[8]	43800 cm^{-1} (5.43 eV) 46000 cm^{-1} (5.71 eV)	MCSCF and MR-ACPF	1998
Nakao *et al.*[9]	129.2 kcal mol^{-1} 45190 cm^{-1} (5.60 eV) 128.2 kcal mol^{-1} 44840 cm^{-1} (5.56 eV)	SA-CASSCF and B3LYP	2001
This work	49158 ± 263 cm^{-1}	VMI	2019

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