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Reactions of Nb₂ and Nb₃ with CO, D₂, N₂, and O₂: Reconciling experimental kinetics with density functional theory-calculated reaction profiles

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Calculated energy profiles for the reactions of neutral Nb₂ and Nb₃ metal clusters with CO, D₂, N₂, and O₂ are presented. In each reaction path, both a physisorption energy minimum, where the reactant remains intact, and a chemisorption energy minimum, where the reactant has dissociated, are calculated and linked by saddle points. We calculate branching ratios for the forward (dissociative) and reverse reactions which we compare with the experimental kinetic data. It is found that a combination of average thermal energies and barrier heights leads to wide variation in branching ratios which compares favourably to previously determined experimental reaction rates. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4733287>]

I. INTRODUCTION

The reactivity of niobium clusters has been studied for over two decades, ever since the coupling of laser ablation sources to produce metal clusters with fast-flow, gas-phase reactors.^{1–3} The early predilection for studying niobium clusters was due to a combination of several factors; ease of cluster production, generally high reactivity, ease of ionisation using tunable laser sources, and suitability to mass spectrometric detection of products by virtue of only one naturally occurring isotope. Since the earliest studies, it has been recognised that the reactivity of neutral and ionic niobium clusters can differ remarkably with different small molecules such as D₂, N₂, O₂, and CO. Moreover, the reactivity of a particular niobium cluster, Nb_n, with a molecule can vary by several orders of magnitude with the addition of just one atom, i.e., Nb_{n+1}. Such variations were found to exist for other cluster reactions (e.g., Co_n + D₂) and provided some of the first evidence that metal clusters possess properties that depend dramatically upon cluster size, which would eventually spawn the concept of nanocatalysis.⁴

Reactivity studies of niobium clusters with CO under fast-flow reaction conditions (assuming pseudo-first-order association reaction kinetics, where [Nb_n] ≪ [gas] ≈ 1–10 Torr) show that the reaction rate generally increases with cluster size, Nb_n (*n* > 2), but notably Nb₂ does not seem to react at all.^{1,5–8} Reactions of Nb_n clusters with CO in pickup cell experiments (at low pressure, ≈ μTorr) give generally similar results.⁹ The reaction of Nb_n with O₂ occurs at essentially the gas-kinetic collision rate and is invariant to cluster size, although the reaction of Nb₂ is slightly slower.⁷

The reactivity results for N₂ and D₂ are quite different from that observed for O₂ and CO; in reactions with N₂ and D₂, the measured rate coefficients with Nb_n (*n* = 2–20) clusters are shown to vary by over three orders of magnitude,^{1,7} with conspicuous low reactivity being observed at Nb₂, Nb₈, and Nb₁₀. As cluster size is varied, there is an apparent correspondence between low reactivity and high ionisation potential and thus a correlation between charge transfer ability and reactivity was initially proposed.¹⁰ However, the fact that similar reactivity is also observed for cationic and anionic clusters suggests that the reactivity variation is more subtle than simple charge transfer.^{6,11–13} Compounding the investigation of niobium cluster reactivity was also the early realization that several niobium clusters display reactivities that indicate the presence of structural isomers. These effects were seen for Nb₁₁, and Nb₁₉ cations reacting with H₂,¹³ and also Nb₉, Nb₁₁, and Nb₁₂ neutral clusters reacting with D₂ and N₂,¹² indicating an important role for geometric structure in cluster reactivity.

To further explore the unusual reactivity patterns observed for N₂ and D₂ reactivity, Bérces *et al.* extensively investigated their interactions with Nb_n clusters (*n* = 2–20), including temperature dependence, and density functional theory (DFT) and extended Hückel molecular orbital calculations.⁷ The reactions with D₂ and N₂ show inverse (negative) temperature relationships for most clusters but not for Nb₂ (D₂ and N₂), Nb₈ (D₂), Nb₁₀ (D₂), and Nb₁₆ (D₂ and N₂). This observation led to the proposition of a double potential well model for these reactions whereby the interaction begins with an initial (reversible) physisorption state that precedes a small barrier before the molecule dissociates to form a strongly bound (irreversible) chemisorption state which is the global minimum. Such a double well model is well established in molecule-surface interactions^{14,15} and has been discussed more generally for cluster-small molecule reactivity in a comprehensive review article by Knickelbein.³ The double well model is also well established in ion-molecule

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reaction systems.^{16–18} The theoretical analysis by Bérce *et al.* concluded that the reaction of Nb_n clusters with D_2 and N_2 was dictated by interaction with an Nb_2 moiety and that the reaction requires charge transfer into ionic potentials, generating energy barriers for molecular dissociation. Although this model has a dependence on an effective ionization potential (IP), similar to the charge transfer theory, the model is not globally consistent with different metal clusters.³

Soon after, the reactivity of Nb_n^+ ($n = 4\text{--}16$) cations with H_2/D_2 was explored as a function of reactant pressure and temperature under very low pressure conditions using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry; the rate of Nb_3^+ was found to be too slow to be detected.^{19,20} The observed rate constants exhibit fall-off behavior with decreasing pressure, consistent with a reversible association reaction for all clusters. An inverse temperature dependence was also observed, which was more pronounced for $n = 8, 10, 11$, and 16 , suggesting that the relative low reactivity of these clusters is due to activation barriers rather than low adsorption energies.

As part of a larger reactivity study of Nb_n ($n = 3\text{--}11$) with H_2 and CO , Bernstein and co-workers recently observed that the reactivity of the neutral Nb_8 cluster with CO was different from other cluster sizes.²¹ Their DFT calculations for $\text{Nb}_8 + \text{CO}$ identified a long-lived intermediate, due to a relatively high saddle point, containing a molecularly bound CO group which predisposed the cluster to further reaction with hydrogen to form CH_3OH . Using simplified Rice-Ramsperger-Kassel (RRK) theory, they calculated an intermediate precursor lifetime of $16\ \mu\text{s}$, orders of magnitude longer than for the other Nb_n clusters.

This reconciliation between experiment and a DFT-calculated high energy barrier by Bernstein and co-workers prompted us to investigate whether the long-known difference in reactivity between Nb_2 and Nb_3 with D_2 , N_2 , O_2 , and CO can be similarly explained and so we embarked on a detailed exploration of the potential energy profiles for these reactions. We have previously worked on the $\text{Nb}_3 + \text{CO}$ reaction and shown that the CO group is dissociated in the global minimum.^{8,22} We use the same approach to calculate the potential energy surfaces of the aforementioned reactions and calculate branching ratios for the forward (dissociative) and reverse reactions which we compare with the experimental kinetic data. This body of work is consistent with our overall general approach of utilising computational studies to provide insight into experimental work. In this case, it is to elucidate the dominant factors at play in order to pro-

vide a fundamental understanding of metal cluster reactivity that is still surprisingly deficient for these simple prototypical systems.

II. COMPUTATIONAL METHOD

The reaction pathways for each stoichiometry were determined using our previously developed Kick-fragment²³ method. The metal cluster was always retained as a bound fragment, and each reactant was kicked both as a fragment and as its constituent atoms. Saddle points linking pairs of minima were located using quasi-synchronous transit calculations and confirmed by intrinsic reaction co-ordinate calculations. These calculations employed the B3P86 hybrid exchange-correlation functional and all atoms were described using the Stuttgart relativistic small core (SRSC) basis set.²⁴ Niobium atoms had core electrons up to and including the third shell treated by an effective core potential.²⁵ This combination of density functional and basis set has been shown to correctly describe qualitative trends in transition metal clusters, whilst being computationally expedient.²² The lowest four multiplicities were “kicked” independently but only the low-energy multiplicities were retained for further calculations.

Once the geometries comprising each reaction path were determined, they were reoptimized using the B97D (Ref. 26) functional. In these calculations, non-metal atoms were treated using Dunning’s aug-cc-pVTZ basis set,^{27,28} retaining the use of SRSC on niobium atoms. B97D has been shown to be accurate for computing cluster geometries and energetics of reactions involving metal centres and it reproduces the reaction profile of $\text{Nb}_2 + \text{N}_2$ as calculated by Bérce *et al.*⁷ which is discussed below (see Secs. III B 4 and III C). Energies, including zero-point energy were extracted directly from the GAUSSIAN 09 (Ref. 29) output.

The structure of each reactant (viz. D_2 , CO , N_2 , and O_2) and the “bare” clusters, Nb_2 and Nb_3 , was optimized by the same method and basis set; energies (including zero-point correction), bond lengths, and harmonic vibrational frequencies are shown in Table I. Energies of all structures are shown in the supplementary material.³⁰

The reference energy for each cluster is the sum of the energies of the metal cluster and the reactant (viz. D_2 , CO , N_2 , or O_2). Basis set superposition error was determined to be minimal and was disregarded in all calculations.

As in our previous study,²² for each reaction we identify the species that has the least interaction between the metal

TABLE I. Calculated properties of the gas-phase reactant molecules.

Reactant	Electronic state	E + ZPE (a.u.)	Bond length (Å)	Harmonic vibrational frequency (cm^{-1})
D_2	$1\ \Sigma_g^+$	− 1.189462	0.745	3094
CO	$1\ \Sigma^+$	− 113.282595	1.135	2123
N_2	$1\ \Sigma_g^+$	− 109.494510	1.099	2368
O_2	$3\ \Sigma_g^-$	− 150.306356	1.215	1546
Nb_2	$3\ \Sigma_g^-$	− 114.044852	2.124	448
Nb_3	$2\ A_2$	− 171.131676	2.431, 2.431, 2.299	107, 249, 359

cluster and reactant, defined as the structure with the highest reactant (D_2 , CO, etc.) vibrational frequency. This species is termed the “capture species” and is always the first geometry presented in each reaction path.

III. RESULTS AND DISCUSSION

A. Nb_2 and Nb_3

The electronic configuration of the niobium atom is $4d^45s^1$, thus Nb_2 is an even-electron species. We calculate the lowest energy state of Nb_2 to be a triplet state with a bond length of 2.124 Å and electron configuration of $1\sigma_g^21\pi_u^42\sigma_g^21\delta_g^2$. The singlet and quintet states lie higher in energy by 0.37 and 1.29 eV, respectively. Our structure is similar to that calculated by Bérces *et al.* using DFT.⁷ Balasubramanian and Zhu undertook first-order configuration interaction (FOCI) and first-order + multi-reference (FO+MR)CI calculations on Nb_2 and Nb_2^+ .³¹ They identify a $^3\Sigma_g^-$ ground state having a bond length of 2.156 Å at the FOCI level and 2.164 Å at the (FO+MR)CI level. Our DFT electronic configuration is the same as the FOCI leading configuration of their ground state, $1\sigma_g^21\pi_u^42\sigma_g^21\delta_g^2$, which comprises 78.6% of the total wavefunction. These calculations are all consistent with experimental results on Nb_2 which identifies the ground state as $^3\Sigma_g^-$.^{32,33}

There are numerous previous calculations of the Nb_3 cluster. We have previously^{8,22} reported calculations using the B3P86 density functional and either the LANL2DZ or SRSC basis sets, both of which yielded a C_s minimum of doublet multiplicity. Goodwin and Salahub,³⁴ Gronbeck *et al.*,³⁵ and Calaminici and Mejia-Olvera³⁶ all report a C_{2v} geometry possessing two long sides and one short (i.e., an acute isosceles triangle). Fowler *et al.*³⁷ also predict a C_{2v} minimum structure, a 2B_1 state with bond lengths of 2.348 (× 2) and 2.472 Å. They also calculate a 2A_2 saddle point with bond lengths of 2.442 (× 2) and 2.287 Å, the energy of this state being only 0.01 kcal mol⁻¹ (4×10^{-4} eV) above their 2B_1 minimum. They show that the imaginary frequency of this 2A_2 state is a b_2 mode that converts between equivalent 2B_1 minima and that the ground state of Nb_3 is therefore of a highly fluxional nature.

Using B97D and the SRSC basis set we find a doublet C_{2v} acute minimum with bond lengths of 2.431 (× 2) and 2.299 Å (apical angle of 56.4°), which very closely matches Fowler’s saddle point structure. The electronic configuration of this state is $\cdots 9a_2^25b_2^24b_1^21a_2^22a_2^1$, leading to a 2A_2 electronic state symmetry. We also locate a saddle point structure with 2B_1 electronic state symmetry only 5×10^{-3} eV (0.1 kcal mol⁻¹, or 40 cm⁻¹) above our 2A_2 minimum, with bond lengths of 2.344 (× 2) and 2.468 Å. The electronic occupation of this state is $\cdots 9a_2^25b_2^23b_1^23b_1^11a_2^22a_2^2$, inspection of the imaginary frequency indicates that this saddle point links equivalent 2A_2 minima ($\nu_{imag} = 95$ cm⁻¹).

Majumdar and Balasubramanian undertook B3LYP and multi-reference configuration interaction (MRCI) calculations on the niobium trimer.³⁸ At the DFT level, they likewise calculate nearly iso-energetic 2B_1 and 2A_2 structures. At the MRCI level the leading configuration of the

2A_2 state is $\cdots 9a_2^25b_2^24b_1^21a_2^22a_2^1$, but this configuration comprises only 61% of the total wavefunction. Similarly they show that the leading configuration of the 2B_1 state $\cdots 9a_2^25b_2^23b_1^23b_1^11a_2^22a_2^2$ composes only 69% of the total wavefunction for that state, suggesting that the ground state of Nb_3 is highly multireference in nature. Both of these leading configurations agree with the electronic configurations of the UB97D/SRSC geometries in the present work. Their detailed analysis of several low-lying electronic states show that only the 2A_1 , 4B_1 , and 6A_1 states of Nb_3 maintain D_{3h} symmetry, other states are subject to Jahn-Teller distortion. The Raman spectrum obtained by Lombardi *et al.*³⁹ indicates a nearly D_{3h} structure, with their analysis of the spectrum suggesting a maximum distortion of the apical angle of 1.7°. The apical angles of the 2A_2 and 2B_1 states calculated in the present work are 56.4 and 63.5°, respectively, i.e., distortions of 3.6 and 3.5° from the ideal 60° angle. The evidence shows that the zero-point-energy motion interconverts Nb_3 between the C_{2v} and D_{3h} geometries. The observed experimental structure is a vibrational average of these geometries.

B. Reaction energy profiles

1. $Nb_3 + CO$

The reaction path for Nb_3CO has been reported by us twice previously, using the B3P86 functional and either the LANL2DZ or SRSC basis set.^{8,22} As in these previous works, the doublet ($S = 1/2$) multiplicity is the lowest in energy, with all higher multiplicities lying significantly higher in energy. Figure 1 shows this reaction pathway, calculated using B97D. The profile of the reaction pathway is similar to that previously reported by us using the B3P86 functional, showing three minima representing associatively and dissociatively bound CO, the latter being the global energy minimum, although the B3P86 derived binding energies are approximately 1 eV greater. The two associatively bound species, **1-I** and **1-III**, represent the CO molecule interacting “head-on” and “side-on” with the Nb_3 face, respectively. Saddle point, **1-II*** converts between these two orientations. In our previous work we have identified a capture species (**1-I**) where the cluster has least interaction with CO as determined by the highest CO vibrational frequency and that also represents the more likely interaction orientation. The saddle point

FIG. 1. Stationary points on the Nb_3CO potential energy surface for the doublet multiplicity. Reported energies are relative to energy of the separated reactants and are given in eV, saddle points are indicated with an asterisk.

FIG. 2. Stationary points on the Nb_2CO potential energy surface for the energetically competitive multiplicities. The black line represents the triplet state and the green line represents the singlet state. Reported energies are relative to the energy of separated triplet Nb_2 and singlet CO and are given in eV, saddle points are indicated with an asterisk.

1-IV* has a similar structure (i.e., the CO molecule is oriented across the Nb_3 face) and provides a small barrier to the global energy minimum dissociative structure (**1-V**).

2. $\text{Nb}_2 + \text{CO}$

The reaction path for Nb_2CO is presented in Figure 2, which shows the triplet and singlet profiles as black and green lines, respectively. Both associative (**2-I** and **2-III**) and dissociative (**2-V**) minima were identified, with the lowest energy minimum being the triplet dissociative structure. These are linked by two saddle points (**2-II*** and **2-IV***). The most significant feature of this reaction pathway is that all species, except the capture species and global minimum, are higher in energy than the separated reactants. The saddle point (**2-II***), corresponding to “twisting” the CO molecule prior to dissociation, is the highest energy structure presented, at 0.68 eV ($S = 1$). On the singlet surface, the highest energy saddle point is **2-IV*** at 0.57 eV above the energy of the separated reactants.

3. $\text{Nb}_{2,3} + \text{D}_2$

Figure 3 shows the doublet reaction path for Nb_3D_2 . A similar quartet path was identified but found to be significantly higher in energy. The lowest energy minimum (**3-V**) is a dissociatively bound structure with the two D atoms bound

FIG. 3. Stationary points on the Nb_3D_2 potential energy surface for the doublet multiplicity. Reported energies are relative to the energy of the separated reactants and are given in eV, saddle points are indicated with an asterisk.

FIG. 4. Stationary points on the Nb_2D_2 potential energy surface for the singlet multiplicity. Reported energies are relative to the energy of the separated reactants and are given in eV, saddle points are indicated with an asterisk.

to opposite faces of the Nb_3 plane. The only associatively bound structure is a structure (**3-I**) that is 0.21 eV below the energy of the separated reactants. The saddle point leading from this structure (**3-II***) is analogous to the first saddle point of the $\text{Nb}_3 + \text{CO}$ reaction (viz. **1-II***) and the motion of the imaginary frequency corresponds to one of the hydrogen atoms moving across the Nb_3 face. Both the geometry and energy of this structure are quite close to that of **3-I**, suggesting that dissociation of D_2 occurs in a facile manner and that the symmetric minimum bound by 1.17 eV, (**3-III**), is the first true minimum in this pathway. The second saddle point (**3-IV***) is a planar structure linking this minimum to the global minimum at -1.50 eV (**3-V**), where the D atoms are bound on opposite faces of the Nb_3 trimer.

The reaction path for Nb_2D_2 is shown in Figure 4. The lowest energy minimum, **4-V**, is a dissociatively bound singlet structure bound by 1.04 eV. A similar triplet structure was identified approximately 0.5 eV higher in energy, but no other triplet minima were identified. These dissociative minima were the only structures identified that had energies below the energy of the separated reactants. On the singlet surface, both associative (**4-I**, connected to the reactants by a dotted line) and dissociative (**4-III**) minima were identified, linked by saddle points **4-II*** and **4-IV***. As in the CO case, D_2 initially binds to a single niobium atom and undergoes a “twisting” movement prior to dissociation. Compared to the $\text{Nb}_2 + \text{CO}$ pathway, however, dissociation occurs much earlier, as the intermediate geometry, **4-III**, does not possess a D_2 unit.

4. $\text{Nb}_{2,3} + \text{N}_2$

Two reaction paths for $\text{Nb}_3 + \text{N}_2$ are presented in Figure 5, which shows the doublet multiplicity. The quartet paths were also calculated, however, they were higher in energy. The first pathway, presented from left to right, (structures **5-I** to **5-VI**) reaches the global minimum, **5-VI**. The second pathway, from right to left (structures **5-VII** to **5-IX**), reach a minimum, **5-IX**, that possesses C_{2v} symmetry.

On the first pathway, three associatively bound minima (**5-I**, **5-II** and **5-IV**) were located, including two nearly iso-energetic candidates for the capture species (**5-I** and **5-II**, connected by a dotted line) that may be considered as a “perpendicular” and “parallel” landing of the N_2 molecule on the Nb_3 plane. The first saddle point on this pathway, **5-III***, represents the N_2 molecule rotating from a position above a Nb_2 bond to being centred over the Nb_3 plane. It is only in the second saddle point, **5-V***, that the N_2 bond is broken.

FIG. 5. Stationary points on the Nb_3N_2 potential energy surface for the doublet multiplicity. Reported energies are relative to the energy of the separated reactants and are given in eV, saddle points are indicated with an asterisk.

The second pathway, leading to the C_{2v} **5-IX**, shown from right to left in Figure 5 is a somewhat more direct pathway, beginning with a sideways approach of N_2 over a Nb_2 bond, leading to structure **5-VII**. There are two things of note in this structure; first that it is bound by only 0.72 eV, a value similar to either of the capture species in the first pathway (viz. **5-I**, -0.75 eV and **5-II**, -0.73 eV), and second, that one nitrogen atom is bound in the Nb_3 plane. The saddle point, **5-VIII***, breaks this planar arrangement ($\phi_{\text{N-Nb-Nb-N}} = 165^\circ$) and the N_2 bond. The second saddle point on this pathway, **5-X***, converts between structures **5-IX** and our global minimum, **5-VI**, by way of a large amplitude motion of the “beneath-face” nitrogen atom.

Yang *et al.*⁴⁰ obtained a zero-electron kinetic energy spectrum of Nb_3N_2 and undertook complementary calculations using several density functionals which indicated a C_{2v} minimum, equivalent to structure **5-IX**. In addition, this minimum was proposed as the global minimum by Bérces *et al.*,⁷ whose DFT calculations identified a global minimum structure bound by 3.2 eV (-311.2 kJ/mol) with doublet multiplicity and C_{2v} symmetry, which has two N atoms split across a common Nb–Nb bond forming a planar N–Nb–Nb–N motif. We have also studied this structure, calculated using the B3LYP density functional, at the complete active space self-consistent field (CASSCF) and MRCI levels of theory.⁴¹

The reaction path for $\text{Nb}_2 + \text{N}_2$ is shown in Figure 6. The singlet (black) and triplet (red) multiplicities are shown. The singlet and triplet pathways begin and end with similar structures that are almost iso-energetic, with the triplet lying 0.009 and 0.016 eV above the singlet for the structures **6-I** and **6-VII**, respectively. However, the barrier to N_2 dissociation on the triplet pathway rises above the energy of the separated reactants, and therefore, we discuss the singlet pathway here. In a similar manner to the $\text{Nb}_3 + \text{CO}$ and $\text{Nb}_3 + \text{N}_2$ pathways, the early part of the pathway converts an “upright” oriented N_2 molecule, **6-I**, to a parallel, **6-III** orientation (relative to Nb_2). These two minima are joined by a quasi-planar saddle point, **6-II***. From **6-III**, the N_2 molecule twists, via saddle point, **6-IV***, to orient perpendicular to the Nb dimer, **6-V**. In this structure, 0.09 eV above the energy of the separated reactants, the N–N distance is 1.494 Å and $\phi_{\text{N-Nb-Nb-N}} = 53^\circ$. In

saddle point, **6-VI***, the N_2 bond is completely broken, with an N–N distance of 1.925 Å and $\phi_{\text{N-Nb-Nb-N}} = 72^\circ$. The global minimum, **6-VII**, is bound by 2.63 eV (singlet) or 2.62 eV (triplet). Bérces *et al.*⁷ also presented DFT calculations for the $\text{Nb}_2 + \text{N}_2$ reaction. They report several associative structures, with “end on” and “side-on” structures of singlet and triplet multiplicities. They calculate a small barrier, which separates lower energy dissociative structures which are similar to ours, the only difference being that their global energy minimum is a quintet state (${}^5B_{1g}$) with D_{2h} symmetry at -2.98 eV (-287.1 kJ/mol). We identify the same structure as the lowest energy quintet, however, we calculate it to be significantly higher in energy than the similar singlet or triplet structures.

5. $\text{Nb}_{2,3} + \text{O}_2$

The reaction path for $\text{Nb}_3 + \text{O}_2$ is shown in Figure 7, and occurs on the doublet surface. The capture species for this reaction, **7-I**, is μ^2 -bound and unlike all other capture species, it has an already significantly perturbed reactant, with an O–O bond length of 1.466 Å. The O–O bond is further lengthened in the nearly iso-energetic saddle point, **7-II***, which possesses an O–O bond length of 1.600 Å. Beyond this saddle point are two highly stable minima, **7-III** and **7-V**, and saddle points, **7-IV*** and **7-VI***, all bound by over 7 eV. The global

FIG. 6. Stationary points on the Nb_2N_2 potential energy surface for the energetically competitive multiplicities. The black lines represent the singlet state and the red lines represent the triplet state. Reported energies are relative to the energy of separated triplet Nb_2 and singlet N_2 and are given in eV, saddle points are indicated with an asterisk.

FIG. 7. Stationary points on the Nb_3O_2 potential energy surface for the doublet multiplicity. Reported energies are relative to the energy of the separated reactants and are given in eV, saddle points are indicated with an asterisk.

minimum, **7-VII**, bound by 8.62 eV, possesses one oxygen atom μ^1 -bound and the second μ^2 -bound in the Nb_3 plane. This is the same global minimum structure as identified by Zhai *et al.*⁴² by photoelectron spectroscopy and concomitant B3LYP calculations. The second C_1 isomer that they proposed as being iso-energetic with the global minimum structure was also identified by us using the B3P86 functional, however, direct optimisation of this structure using B97D returned structure **7-VII**. We also identify a low-energy, C_s , isomer, 0.32 eV above the global minimum (**7-V**); this structure is similar to a third isomer reported by Zhai *et al.*, which they calculate to be 0.08 eV above their global minimum.

Two capture species were discovered for the reaction of $\text{Nb}_2 + \text{O}_2$ and reaction paths beginning with both species are shown in Figure 8, both reaction paths occur on the singlet surface and lead to the same minimum structure, **8-III**, at -8.09 eV. The first reaction path, drawn from left to right (structures **8-I** to **8-III**), begins with a capture species, **8-I**, bound by 3.22 eV, where the Nb_2 dimer and O_2 molecule meet oriented perpendicular to each other. The O_2 bond is

FIG. 8. Stationary points on the Nb_2O_2 potential energy surface for the singlet multiplicity. Reported energies are relative to the energy of the separated reactants and are given in eV, saddle points are indicated with an asterisk.

simply cleaved over a small transition barrier, **8-II***. In the second reaction path, from right to left, structures **8-IV** to **8-III** correspond to the Nb_2 dimer and O_2 molecule meeting parallel to each other to form a planar capture species, **8-IV**, which is bound only slightly more strongly than **8-I**, at 3.35 eV. The O_2 molecule is broken in a barrierless step to yield two oxygen atoms bound to the Nb dimer, **8-V**, which is bound by 7.39 eV. This structure forms the global minimum, **8-III**, via saddle points, **8-VI*** and **8-VIII***, and intermediate **8-VII**. This intermediate structure has C_{2v} symmetry and $\phi_{\text{O-Nb-Nb-O}} = 101^\circ$.

C. Kinetic analysis

From the generated reaction profiles we can reduce all the surfaces to a very simplified reaction scheme

where the intermediate corresponds to the capture species. The forward rate coefficient, k_f , can be taken to correspond to the slowest (rate-determining) forward reaction step, which is passage over the highest barrier, and the backward rate coefficient, k_b , corresponds to reformation of separated reactants. Note that there is a variational or loose transition state^{17,43} for the barrierless processes of forming the capture species, or reforming the separated reactants.

The rate coefficient for the overall reaction is then given by

$$k_{\text{rxn}} = k_{\text{coll}}\phi, \quad (2)$$

where ϕ is the forward branching ratio, which in the simplified reaction scheme is approximated by

$$\phi = \frac{k_f}{k_b + k_f}. \quad (3)$$

When the energy of the reactants is higher than all other structures (i.e., exothermic reaction), then $k_b/k_f \rightarrow 0$, $\phi \rightarrow 1$ and therefore $k_{\text{rxn}} \approx k_{\text{coll}}$. In this situation, as the temperature increases both k_b and k_f increase, however, since the former is much smaller its proportional increase is larger so ϕ decreases. This explains the negative (inverse) temperature dependence observed for some systems, even for highly exothermic reactions.^{16,18,44}

From Rice-Ramsperger-Kassel-Marcus (RRKM) theory and assuming the harmonic classical limit, the energy dependence of a reaction reduces to the following expression:

$$\begin{aligned} k(E) &= \frac{\int^E \rho^\ddagger(\epsilon) d\epsilon}{h\rho(E - E_{\text{well}})} \rightarrow \frac{\prod_{i=1}^{3N-6} h\nu_i}{h \prod_{i=1}^{3N-7} h\nu_i^\ddagger} \frac{(E - E^\ddagger)^{3N-7}}{(E - E_{\text{well}})^{3N-7}} \\ &= v_n \left(\frac{E - E^\ddagger}{E - E_{\text{well}}} \right)^{3N-7}. \end{aligned} \quad (4)$$

This is the same result as RRK theory, where E_{well} is the energy of the capture species relative to the energy of the separated reactants, E is the sum of the average kinetic and rovibrational energies of the separated reactants, $E^\ddagger$ is the energy of the transition-state relative to the energy of the separated reactants, $(E - E^\ddagger)$ is the available energy for passage over the transition-state energy, and $(E - E_{well})$ is the total energy of the system relative to the energy of the capture species. The transition state can either be the tight transition state, corresponding to the highest barrier, for the forward reaction, or the loose (variational) transition state for the backward reaction to reform the separated reactants. Note that E is the average energy and does not provide information about the real distribution of translational, vibrational, and rotational energies. The available energy for the reverse reaction passage via the variational transition state depends on where that state is located and how much energy is locked in rotations, via conservation of angular momentum, as vibrations change to rotations for the reverse reaction. However, it can be approximated to the available energy for the reverse reaction, E , the energy of the system above the separated species. So the branching ratio can now be written

$$\phi(E) = \frac{\nu_f \left(\frac{E-E_0}{E-E_{well}} \right)^{3N-7}}{\nu_b \left(\frac{E}{E-E_{well}} \right)^{3N-7} + \nu_f \left(\frac{E-E_0}{E-E_{well}} \right)^{3N-7}}, \quad (5)$$

where E_0 is the (highest) barrier from the capture species to dissociation, relative to the energy of the separated reactants (i.e., it is negative if it lies below the energy of the reactants).

If the reaction path is not highly curved, then the vibration of the bound capture species that corresponds with the reaction coordinate is the same for both the forward reaction coordinate and the backward (reverse) reaction coordinate and the relationship becomes

$$\phi(E) = \frac{\left(\frac{E-E_0}{E} \right)^{3N-7}}{1 + \left(\frac{E-E_0}{E} \right)^{3N-7}}. \quad (6)$$

Note that since the $(E - E_0)$ terms refer to the energy available for passage over the transition-state energy and comes from the sum of states, if the transition-state energy exceeds the total energy of the system, then the available energy becomes zero. Therefore, as the highest energy barrier, E_0 , becomes more negative, the branching ratio approaches 1 and the reaction rate becomes the same as the collision rate. If the barrier lies above the energy of the separated reactants, and approaches the available internal energy E , then ϕ will tend towards zero. Intermediate E_0 values will have ϕ values in between zero and one.

Our following analysis of the potential energy surfaces uses this ratio of the branching to provide a qualitative prediction about the rate of the overall reaction, k_{rxn} , which can be compared with the experimental values. Here E is taken to be the sum of internal energy of the reactants, which includes centre of mass kinetic energy (E_k) and vibrational energy (E_v) contributions. $\phi(E)$ should be averaged over thermal distributions of E_k and E_v . However, since the spread of thermal reactions is small compared to $(E - E_{well})$, and also

TABLE II. Calculated parameters for reactions of Nb₂ and Nb₃ with CO, H₂, N₂, and O₂ as discussed in the text. The qualitative predicted rate is given as fast, moderate, slow, or no reaction.

	TS	S	E ₀ (eV)	φ(E)	Predicted rate	k _{exp} (10 ¹¹ cm ³ s ⁻¹) ^a
Nb ₃ + CO	1-IV*	1/2	-0.90	1.00	Fast	0.52 ^b
Nb ₂ + CO	2-II*	1	+0.68	0	No	0 ^b
Nb ₂ + CO	2-IV*	0	+0.16	0.1	Slow	0 ^b
Nb ₃ + D ₂	3-II*	1/2	-0.20	0.92	Fast	2.0
Nb ₂ + D ₂	4-II*	0	+0.21	0.05	Slow	0.05
Nb ₃ + N ₂	5-III*	1/2	-0.56	1.00	Fast	5.7
Nb ₃ + N ₂	5-VIII*	1/2	-0.39	1.00	Fast	5.7
Nb ₂ + N ₂	6-VI*	0	-0.01	0.53	Mod	0.034
Nb ₂ + N ₂	6-VI*	1	+0.53	0	No	0.034
Nb ₃ + O ₂	7-II*	1/2	-3.19	1.00	Fast	34
Nb ₂ + O ₂	8-II*	0	-3.00	1.00	Fast	10

^aPseudo-first-order reaction rate (from Ref. 7).

^bReaction rate relative to Nb₃ (from Ref. 1).

small compared to $(E - E_0)$ for most reactions, the thermal distributions are well approximated by microcanonical (single energy) distributions. Following Bernstein and co-workers,²¹ E_k is held constant for all systems at 0.3 eV and E_v is given by $(3N - 6)kT$, which is 0.15 eV and 0.23 eV for the tetra-atomic and penta-atomic systems, respectively, at 298 K. The various parameters and calculated $\phi(E)$ values are tabulated in Table II along with the experimentally observed rate constants, k_{exp} . The rate constants for CO reactions are only given relative to Nb₃, which has a reported value of 1.0.¹

For the reactions of O₂ with Nb₂ and Nb₃, the saddle points are both near -3 eV leading to maximum values of 1 for $\phi(E)$, suggesting very fast forward reactions for dissociation. This is entirely consistent with the observed reactivity rate for O₂ which is observed to occur at the gas-kinetic collision rate.⁷ The experimentally observed difference of $\times 3$ between Nb₃ and Nb₂ is not reflected in the value for $\phi(E)$ but is due to the larger collision cross section (and collision rate) for Nb₃.

The reaction of Nb₂ + CO occurs on two energetically competitive surfaces, singlet and triplet. Given that Nb₂ has a triplet ground state we consider that surface first. From capture species (**2-I**), the reaction proceeds over saddle point **2-II*** which is 0.68 eV above the energy of the separated reactants, leading to a zero $\phi(E)$. As seen in Figure 2, the singlet surface is generally lower in energy with the highest energy saddle point being **2-IV*** at 0.16 eV. The calculated $\phi(E)$ value is 0.1, using the simple kinetic analysis with a single rate-determining step for the forward reaction. Since the singlet-surface saddle points, **2-II*** and **2-IV***, are similar in energy, it can be expected that passage over these two saddle points are both rate determining. Hence, the $\phi(E)$ value would be less than 0.1 if a more sophisticated analysis was to be used, but this would not change the qualitative prediction that the forward (dissociation) reaction on this surface is either slow or too slow to be observed.

Only the doublet surface is competitive for the reaction of Nb₃ + CO and the highest barrier to CO dissociation is structure **1-IV*** at -0.90 eV. The resultant $\phi(E)$ is 1.0, indicating a very fast forward reaction. The values of $\phi(E)$ calculated for

these reactions are largely consistent with the observed rates; experimentally, Nb₂ is not observed to react with CO under any conditions whereas Nb₃ is relatively reactive.

The profile for the reaction between Nb₂ with N₂ is quite different between the singlet and triplet surfaces. Dissociation on the triplet surface occurs at the same structure but at a much higher energy, 0.53 eV, leading to a predicted zero $\phi(E)$. On the singlet-surface dissociation occurs at structure **6-IV***, with energy -0.21 eV and a calculated $\phi(E) = 0.53$. The doublet profile for the Nb₃ + N₂ reaction is all exothermic. The “above face” approach via **5-VIII*** has a barrier at -0.56 leading to $\phi(E) = 1.0$. The approach of the N₂ across a Nb–Nb bond, via **5-VIII***, also has a low barrier of -0.39 eV and implies another fast reaction, with $\phi(E) = 0.99$. The actual reaction rate would be some orientation-weighted- and energy-weighted average of the above-face and across-bond reaction rates, with a predicted $\phi(E)$ of around 1.0. These results indicate that Nb₃ is expected to react more rapidly with N₂ than Nb₂ and this is consistent with experiment with the former being over 100 times faster.

The singlet surface of the Nb₂ + D₂ reaction lies above the energy of the separated reactants until the global minimum, the highest point being structure **4-II*** at $+0.21$ eV. The calculated reaction profile has a positive barrier to dissociation, leading to a calculated $\phi(E) = 0.05$ and suggesting a slow reaction. The Nb₃ + D₂ reaction on the doublet surface is exothermic at all points, with the D₂ molecule dissociating at structure **3-II*** with energy -0.21 eV. Thus, the forward reaction is expected to proceed at a relatively fast rate, $\phi(E) = 0.94$. These results are consistent with experiment, where both reactions occur but the Nb₃ reaction is observed to be 40 times faster than the Nb₂ reaction.

Using extended Hückel calculations, Bérces *et al.* have proposed that barriers exist in the reactions of Nb₂ with H₂ and N₂ due to avoided crossings between neutral and ionic orbital configurations of the same symmetry.⁷ Although their calculations were done assuming a direct linear approach of reactants in a perpendicular bridging orientation, their orbital analysis is supported by atomic charge densities calculated at various minima on the DFT surfaces, which showed significant charge transfer from cluster to the H, or N, atoms as the reaction proceeds. Our calculated Nb₂ + H₂ and N₂ reaction pathways involve similar trajectories (see saddle points **4-IV** and **6-VI**, respectively) and we also calculate significant charge transfer from Nb₂ to the H (-0.12) and N (-0.29) atoms in the global minimum structures, **4-V** and **6-VII**, respectively (see supplementary material³⁰). Therefore, the barriers we calculate for these two reactions arise from the same interactions.

The DFT investigations by Bérces *et al.* into the reactions of Nb₃ with H₂ and N₂ were done using the same linear trajectories into perpendicular bridging configurations across a single Nb–Nb bond, consistent with their DFT calculations of global minima with C_{2v} symmetry. Analysis using this restricted interaction geometry led them to similar conclusions about charge transfer into ionic orbitals and that the third Nb atom acts as a non-participating spectator. However, for Nb₃ reactions, we calculate key saddle point structures that involve interactions of all three Nb atoms with H₂ (**3-II**) and N₂

(**5-III**), although the alternative path of Nb₃ + N₂ (via **5-VIII**) primarily involves only two Nb atoms. For both these reactions, this additional interaction significantly reduces the saddle point barrier and it is effectively this reduction that results in the faster kinetic rates calculated (and observed) for these reactions relative to Nb₂.

It is clear that a quantitative evaluation of reaction profiles between metal clusters and small molecules requires an exploration of the potential energy surface involving full geometric flexibility. The unusually slow reaction kinetics observed for larger niobium cluster (e.g., Nb₈ and Nb₁₀) may well be explained by similar calculation of reaction profiles to identify particularly high barriers, as found by Bernstein and co-workers²¹ for Nb₈ + CO. Similarly, it would be worthwhile to investigate whether the reaction pathways for cationic and anionic clusters display the same characteristics or whether there are other features that give rise to the observed variation in reactivity.

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