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The vibrational excitation of NO desorbing from NiO(100) after UV laser irradiation: is NO^- a possible intermediate species?

T. Klüner^{a,*}, S. Thiel^a, H.-J. Freund^a, V. Staemmler^b

^a Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-14195, Berlin, Germany

^b Ruhr-Universität Bochum, Lehrstuhl für Theoretische Chemie, Universitätsstr. 150, D-44780, Bochum, Germany

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Abstract

We report on ab initio and wave packet calculations with the intention of simulating the vibrational excitation of NO desorbing from a NiO(100) surface after laser irradiation. The influence of the electrostatic field above the singly positively charged surface on the N–O equilibrium distance of the NO^- -like intermediate is investigated by Hartree–Fock calculations. It is shown that the field leads to a considerable shortening of the equilibrium bond length of NO^- , whereas the equilibrium distance of the neutral NO molecule is only slightly modified. Taking this field effect into account, we are able to obtain quantitative agreement between experimental and theoretical vibrational state populations. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Quantum state selective photochemical desorption of NO molecules from metal and metal oxide surfaces has been the subject of experimental studies in the last decade [1–4]. In order to interpret the experimental results and to obtain a microscopic understanding of these DIET (desorption induced by electronic transitions) phenomena, detailed theoretical investigations are essential [5–11]. Many investigations of the dynamics of the nuclear motion have been performed either by solving the classical [12–15] or quantum mechanical equations of motion [6,7,16–19]. However, all dynamical calculations so far have been essentially empirical, because of the

lack of sufficiently accurate multidimensional potential energy surfaces (PES), especially for the excited electronic states. Recently, the first ab initio calculation of a two-dimensional excited state PES has been reported for the system NO/NiO(100) [19]. The excited species has been characterised as a charge transfer state, where an electron is transferred from the surface to the NO molecule, yielding an NO^- -like intermediate [8,20]. Agreement with experimentally observed velocity distributions was obtained using the ab initio PES as the basis for time-dependent three-dimensional wave packet calculations [19].

The existence of an NO^- -like intermediate has been doubted recently [21,22]. If one uses the gas-phase equilibrium distances of NO and NO^- the calculated vibrational excitation of the desorbing NO molecules is much higher than observed experimentally. Therefore, the negative ion model used in many current studies was put into question.

* Corresponding author. Fax: +49-30-84134101.

In the present Letter we show that for the system NO/NiO(100), the negative ion model is indeed in quantitative agreement with experiment as soon as electrostatic effects, which are the consequence of the transfer of one electron from the ionic substrate to the adsorbate, are taken into account.

2. Methods of calculation

In order to investigate the electrostatic effects after charge transfer from the substrate to the adsorbate, restricted open-shell Hartree–Fock calculations (ROHF) for the $^2\Pi$ ground state of NO and the $^3\Sigma^-$ ground state of NO^- above the (100) surface of NiO are performed. The Bochum program package [23–26] was used throughout. For oxygen and nitrogen the 9s5p basis of Huzinaga [27] was employed, contracted to triple-zeta quality and augmented by one diffuse p-set with the exponents 0.05 for nitrogen and 0.06 for oxygen and by one d-set with the exponents 0.98 for nitrogen and 1.28 for oxygen, respectively. The electrostatic effect of the ionic surface is simulated by a semi-infinite Madelung potential of point charges possessing the ionicity ± 2 (unmodified field). In Ref. [20] we showed that the potential energy of an excited charge transfer state, derived from extensive configuration interaction cluster calculations, can easily be modelled by placing the NO^- anion into a modified point charge field, describing the ionisation from an orbital delocalised over all surface oxygen ions of an NiO_5^{8-} cluster. The modified point charge field is constructed by reducing the effective negative charges at the positions of the four surface oxygen ions in the direct neighbourhood of the adsorption site by 0.25 each (called field 2 in Ref. [20]). Within this simplified model, the ground state of the substrate–adsorbate system is described by an NO molecule above the nickel site of the ‘neutral’ Madelung potential, whereas the charge transfer state is simulated by calculating an NO^- molecule above the ‘ionised’ Madelung potential (field 2).

In the present study we have calculated potential energy curves of NO and NO^- as functions of the nitrogen–oxygen distance r for two situations: (a) for a quasi-infinite distance between the molecules and the point charge fields ($R = 900.0$ au) and (b)

for a much shorter distance, which is relevant for laser-induced desorption ($R = 4.0$ au). In the remainder of the Letter, R denotes the distance between the nitrogen atom and the $+2$ point charge of the field representing the Ni^{2+} adsorption site. In all calculations the molecule is tilted by 45° with respect to the surface normal [8].

In order to simulate the vibrational populations, the potential curves of the ground state (NO/neutral field) and the excited charge transfer state (NO^- /field 2) are approximated by harmonic oscillator functions. The relative equilibrium distances and in some studies also the force constants are fitted to the results of the ROHF calculations. The vibrational ground state wave packet $|0\rangle$ of the electronic ground state potential is then vertically transferred to the excited state, where it is propagated in time for a residence lifetime t_n under the influence of the NO^- potential using standard wave packet techniques. The partial vibrational populations $P_v(t_n)$ are obtained by projecting the resulting wave packet on the vibrational eigenfunctions $|v\rangle$ of the NO potential, where \hat{H}_{ex} denotes the excited state Hamiltonian. Of course, in this procedure, we assume a complete separability of the NO vibration from the centre of mass translation. This is a reasonable first approximation, since there is experimental evidence of a decoupling of translation and NO vibration [3].

$$P_v(t_n) = \left| \langle v | e^{-i\hat{H}_{\text{ex}}t_n} | 0 \rangle \right|^2. \quad (1)$$

The resulting partial vibrational populations are averaged according to the procedure introduced by Gadzuk et al. [5] assuming an exponential decay of the negative ion resonance with a resonance lifetime τ :

$$P_v(\tau) = \frac{\sum_{n=1}^{n_{\text{max}}} P_{\text{des}}(t_n) P_v(t_n) \exp\left(-\frac{t_n}{\tau}\right)}{\sum_{n=1}^{n_{\text{max}}} \exp\left(-\frac{t_n}{\tau}\right)}. \quad (2)$$

The resonance lifetime τ has been chosen to be $\tau = 24.19$ fs (1000 au) in order to reproduce a reasonable desorption probability per excitation event [19] of 3.3%. However, our final vibrational state populations are only slightly affected even if τ is varied over a wide range. An increment of $\Delta t_n = 20$ au is chosen and residence lifetimes of $t_n = n\Delta t_n$ up

to a maximum value of $n_{\max} = 400$ are used. The function $P_{\text{des}}(t_n)$ has been obtained from one-dimensional wave packet calculations [28]: the asymptotic square norm of the wavefunction is calculated for a wave packet jumping scenario for each residence lifetime t_n on the ab initio PES [19] for a tilt angle of 45° .

The populations of the vibrational levels can be expressed by an effective temperature using the Boltzmann formula.

$$\ln\left(\frac{P_v}{P_0}\right) = -\frac{E_v - E_0}{kT} \quad (3)$$

3. Results and discussion

As known from previous studies [21,22], wave packet calculations like those described in the previous paragraph yield unphysically high vibrational excitations if the distances of the minima of the two harmonic oscillators are fixed to the equilibrium distances of NO ($r = 2.175$ au [29]) and NO⁻ ($r = 2.377$ au [29]) in the gas phase.

This is shown in Fig. 1, where harmonic oscillator potentials for NO and NO⁻ have been used in the quantum dynamical calculations. Their equilibrium distances are separated by 0.2 au, the force constants are chosen to reproduce the ground vibrational level of the two molecules. It is seen that an oscillatory

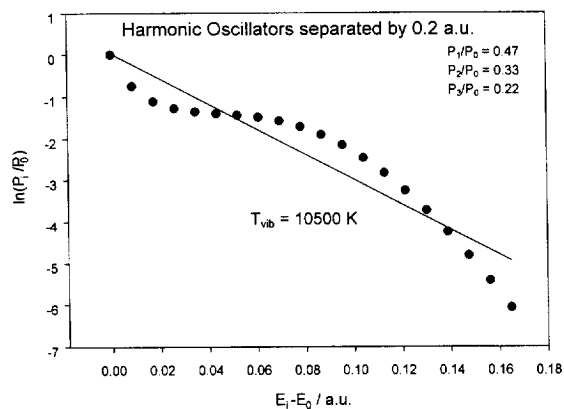


Fig. 1. Boltzmann plot for a simulation of vibrational excitation using the equilibrium distances of NO and NO⁻ in the gas phase (harmonic oscillators separated by 0.2 au).

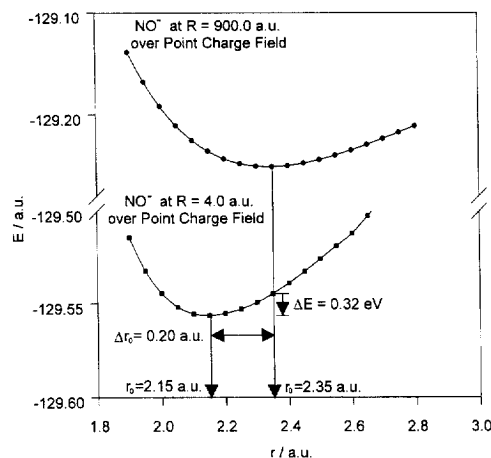


Fig. 2. ROHF potential curves as a function of the internal NO distance r . R denotes the distance of NO⁻ from the field.

behaviour in the Boltzmann plot is obtained, which is far from describing a thermal population. If a straight line is enforced to fit the population vs. energy plot, a temperature of $T_{\text{vib}} = 10500 \text{ K}$ is derived, which is completely different from the experimentally observed value of about $T_{\text{vib}} = 2000 \text{ K}$ in the case of NO/NiO(100) [3]. A physically more meaningful comparison with experiment is based on the relative vibrational populations (theory: $P_1/P_0 = 0.47$, $P_2/P_0 = 0.33$; experiment: $P_1/P_0 = 0.17$, $P_2/P_0 = 0.06$), which are also definitely incompatible. It has been pointed out by several authors [7,21,22] that agreement with the experimental results can be obtained if the separation of the harmonic oscillators is much smaller. It has been argued that the length of the NO bond in the intermediate excited state must be much closer to NO than to NO⁻, which means that only a partial charge transfer into the anti-bonding $2\pi^*$ orbital of the negatively charged species [22] can occur and no NO⁻ intermediate can be formed.

However, as shown in Fig. 2, the N–O equilibrium distance of the NO⁻ anion (with a full negative charge) is markedly contracted if NO⁻ is placed into the electrostatic field above the NiO(100) surface. This contraction of the N–O bond length amounts to as much as 0.2 au if NO⁻ approaches the surface to a Ni–N distance of 4.0 au. As indicated in Fig. 2, the shortening of the bond leads to a stabilisation of 0.32 eV, which is a consequence of the strong electro-

static field above the ionised surface generated directly after the charge transfer of one electron from the oxygen anions to NO.

The diffuse charge distribution of the NO^- molecule is strongly polarised towards the positive charges at the ionised surface. This results in an internal charge transfer of ~ 0.4 electron from oxygen to nitrogen. Table 1 contains the result of a Mulliken population analysis for NO^- at quasi-infinite ($R = 900.0$ au) and short ($R = 4.0$ au) distances from the ionised field 2. A detailed analysis shows that ~ 0.5 electron is transferred from oxygen to nitrogen via the 1π orbital and ~ 0.2 electron is transferred back via the $2\pi^*$ orbital when NO^- is placed in the electrostatic field.

This field-induced redistribution of charge within the NO^- molecule is connected with a bond length contraction, since the character of the 1π orbital changes when the molecule approaches the surface. At infinite distance from the field, the 1π orbital has a dominating contribution of the oxygen atomic orbitals, i.e. it has lone pair character. The field effect and the polarisation of the 1π orbital towards the nitrogen atom yields a molecular orbital with larger contributions of the nitrogen atomic orbitals, i.e. with stronger bonding character. Thus, the field-induced contraction of the N–O bond is attributed to the change in the character of the 1π orbital from non-bonding to bonding.

Similar calculations for the neutral NO molecule above the non-ionised surface show almost no influence of the field on the intramolecular distance. The calculated equilibrium distances are 2.11 au for $R = 900.0$ au, i.e. for NO in the gas phase, and 2.10 au for $R = 4.0$ au.

Table 1

Mulliken populations analysis of NO^- above the ionised point charge field (field 2) as a function of the molecule/field distance ($r(\text{N}-\text{O}) = 2.35$ au)

$R(\text{N}/\text{field})$ (au)	Atom	1π population	$2\pi^*$ population	Net charge
900.0	N	0.85	1.62	-0.36
	O	3.15	0.38	-0.64
4.0	N	1.38	1.45	-0.75
	O	2.62	0.55	-0.25

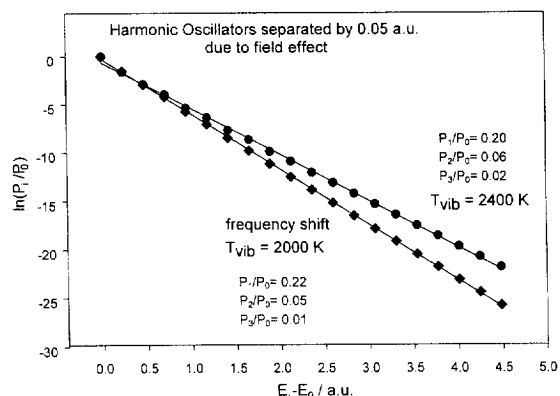


Fig. 3. Boltzmann plot for a simulation of vibrational excitation using equilibrium distances of NO and NO^- with field effects taken into account (harmonic oscillators separated by 0.05 au).

In order to check the influence of this field effect on the vibrational populations we performed subsequent wave packet calculations by setting up two harmonic oscillator potentials with a difference of $2.15 - 2.10$ au = 0.05 au in the equilibrium distances. The force constants of the harmonic oscillators are chosen to match the experimentally observed vibrational frequencies of NO and NO^- in the gas phase, respectively. The results of these calculations are presented in Fig. 3. The Boltzmann plot is linear and yields a vibrational temperature of $T_{\text{vib}} = 2400$ K. The vibrational populations are close to the experimental values. If the change of the force constant of the NO^- molecule due to the field effect is also taken into account by fitting the force constant of the harmonic potential to the calculated potential curve (Fig. 2) the results are only slightly modified ($T_{\text{vib}} = 2000$ K). The vibrational frequency of the neutral NO molecule is almost not affected by the electrostatic field. The vibrational distributions and the frequencies used for the oscillators in the harmonic approximation are summarised in Table 2.

However, the excellent agreement with the experimental data should be regarded with some care. The omission of electron correlation effects in our study results in an underestimation of bond lengths, which is generally the case for Hartree–Fock calculations. The experimental NO^- equilibrium distance in the gas phase is quite well reproduced (only 0.027 au too short), but the NO equilibrium distance shows a

Table 2
Vibrational distributions of the desorbing molecules

Vibrational populations	Experiment [3]	$\Delta r(\text{NO}) = 0.20$ au	$\Delta r(\text{NO}) = 0.05$ au	$\Delta r(\text{NO}) = 0.05$ au
		ω_{gas}	ω_{gas}	ω_{field}
P_1/P_0	0.17	0.47	0.20	0.22
P_2/P_0	0.06	0.33	0.06	0.05
P_3/P_0		0.22	0.02	0.01

Δr denotes the relative difference of the minima of the two harmonic oscillators. ω_{gas} indicates that gas-phase frequencies [29] have been used for NO and NO^- ($\omega_{\text{gas}}(\text{NO}) = 1904 \text{ cm}^{-1}$, $\omega_{\text{gas}}(\text{NO}^-) = 1363 \text{ cm}^{-1}$) in the harmonic approximation. ω_{field} indicates that the frequency of NO^- is modified by taking the field effect into account ($\omega_{\text{field}}(\text{NO}^-) = 1481 \text{ cm}^{-1}$).

larger error (0.065 au too short). If the NO equilibrium distances for the adsorbed NO species are corrected by these values, a much smaller vibrational excitation is expected in our wave packet calculations, because the N–O distance of NO is now quite similar to that of NO^- above the ionised surface.

On the other hand, the electrostatic model for the description of the surface is simplified in the present study. The use of a cluster model, such as NiO_5^{8-} in a point charge field, will result in a smaller polarisation effect, because the Pauli repulsion between the surface oxygen anions and the NO^- molecule will reduce the strong polarisation of the electron cloud of NO^- towards the surface. Therefore, the contraction of the NO^- bond length will be smaller if a more realistic model for the surface is used.

Thus, the excellent agreement between experiment and theory might partly be due to the cancellation of errors. However, the main conclusions of the present study remain unchanged and future cluster calculations will allow for a quantitative analysis.

4. Conclusions

In this Letter, we investigated the vibrational excitation of NO after laser-induced desorption from an NiO(100) surface. By means of ab initio calculations for NO and NO^- these molecules under the influence of the neutral and the ionised oxide surface, respectively, it was found that the difference of the internal equilibrium bond lengths between the adsorbed NO and NO^- species is only ~ 0.05 au and not 0.20 au as in the gas phase. Subsequent wave packet calculations yield vibrational excitations in

excellent agreement with experimental values. We conclude that an ionic intermediate with a full negative charge presents a consistent description of the laser-induced desorption, at least in the case of oxide surfaces, while on metal and semiconductor surfaces a partial charge transfer might take place.

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