

Velocity Distributions after Laser-Induced Desorption of NO from NiO(100)— The Role of the Angular Coordinate

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Abstract. The experimental velocity distributions of NO desorbing from a NiO(100)-surface are simulated using a time-dependent wave packet method. Including the polar angle between the surface normal and the adsorbate molecular axis yields bimodal distributions in the correct velocity range and reasonable desorption probabilities if a resonance lifetime on the order of 25 fs is assumed. For two-dimensional simulations, an angular-independent charge-transfer-state was chosen as excited state in order to investigate the influence of the electronic ground-state on the final state distributions. We compare our results with wave packet calculations using a representative *ab initio* angular-dependent excited-state potential energy surface using a three-dimensional Hamiltonian.

1. INTRODUCTION

The theoretical description of laser-induced desorption has made considerable progress since the early days of Menzel, Gomer, and Redhead, who developed the fundamental ideas of DIET (desorption induced by electronic transitions).^{1,2} Since then, there have been notable advances in characterizing the potential energy surfaces involved in the desorption process as well as in the description of the dynamics of nuclear motion.³⁻¹²

However, a detailed understanding of experimental results still remains a challenge, but much progress has been achieved in the last few years.¹³ Recently, an *ab initio* potential energy surface (PES) for the electronically excited state involved in the desorption process of NO from NiO(100) has been calculated.¹² It turned out that an Antoniewicz scenario⁴ involving NO⁻ as an intermediate results in a consistent description of all experimental data.^{12,14} In the present paper we focus on the interpretation of bimodal velocity distributions obtained during laser-induced desorption of NO from NiO(100) as a well-characterized adsorbate substrate system.¹⁵⁻¹⁷ We address especially the importance of the rotational coordinate for the qualitative understanding of the shape of the distributions which are a basic feature of experimental results.

2. ONE-DIMENSIONAL WAVE PACKET CALCULATIONS

2.1. Computational Methods and Parameters

The wave packet calculations of the nuclear wavefunction were carried out in a discrete representation using an equidistant grid covering a range from 3 au to 14.5 au with 512 gridpoints. This is sufficient to represent a maximum momentum of about 140 au in the interaction region of the potentials. The desorbing part of the wavefunction is separated and propagated in momentum space by the method proposed by Heather and Metiu¹⁸ with the transfer function

$$f_{trans} = 1 - \frac{1}{1 + \exp\left(\frac{a}{\hbar} \cdot (z - z_{trans})\right)}$$

with $a = 6.0$ au and $z_{trans} = 12.6$ au. (1)

The time evolution $\psi(t) = \exp\left(-\frac{i}{\hbar} \cdot \hat{H} \cdot t\right) \cdot \psi(t=0)$ was calculated by expanding the time evolution operator $\hat{U}(t) = \exp\left(-\frac{i}{\hbar} \cdot \hat{H} \cdot t\right)$ in a basis of complex Chebyshev polynomials $\Phi_n(\hat{X})$ with the Hamiltonian as an argument.^{19,20}

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We performed a wave packet jumping procedure, in which the rotational vibrational ground-state wave packet of the electronic ground state is transferred vertically to the excited-state PES. After certain fixed residence-times t_n of the excited wave packet it is vertically quenched and propagated on the ground-state potential until the desorption probability (the asymptotic square norm of the wave packet) is converged as a function of propagation time. This is generally the case after a total simulation time of about 1.5 ps.

According to Gadzuk,^{21,22} any general observable $A(t_n)$ resulting from such a wave packet jumping procedure is calculated by performing a stochastic averaging procedure. Assuming an exponential decay of the excited-state population, the only parameter in this approach is the lifetime τ of the negative ion resonance

$$A(\tau) = \frac{\sum_{n=1}^N A(t_n) \cdot \exp\left(-\frac{t_n}{\tau}\right)}{\sum_{n=1}^N \exp\left(-\frac{t_n}{\tau}\right)} \quad (2)$$

The index n accounts for the quantum trajectory with the fixed residence-time t_n . The resonance lifetime τ can be interpreted as the spectroscopic lifetime of the negative ion resonance. In the one-dimensional approach, up to 500 different residence-times t_n , separated by $\Delta t = 100$ au were used in the averaging procedure of eq 2. This high value of $N = 500$ guarantees a converged result in case of all chosen values of the resonance lifetime τ (see below).

2.2. The Potentials

The potential energy configuration in the one-dimensional calculations consists of a ground-state $V_{gr}(z)$ and an excited charge-transfer-state $V_{ct}(z)$, as shown in Fig. 1. The potential energy curve of the charge transfer-state results from ab initio calculations using a NiO_5^{8-} cluster embedded in a Madelung field using an extended configuration interaction approach.²³ It turns out that a transfer of one electron from the substrate to the adsorbate results in a NO^- like intermediate, for which the desorption scenario is Antoniewicz-like.

In this study, the one-dimensional curve resulting for a fixed adsorption geometry with a 45° angle with respect to the surface normal was chosen. An analytical fit to the complete two-dimensional potential energy surface can be found elsewhere.¹²

The ground-state V_{gr} is a one-dimensional version of the slightly modified two-dimensional potential energy surface of Smedley et al.²⁴ It was originally derived from experimental data of NO scattering from a $\text{Ag}(111)$ surface.²⁵ Again, the 45° curve was constructed to repro-

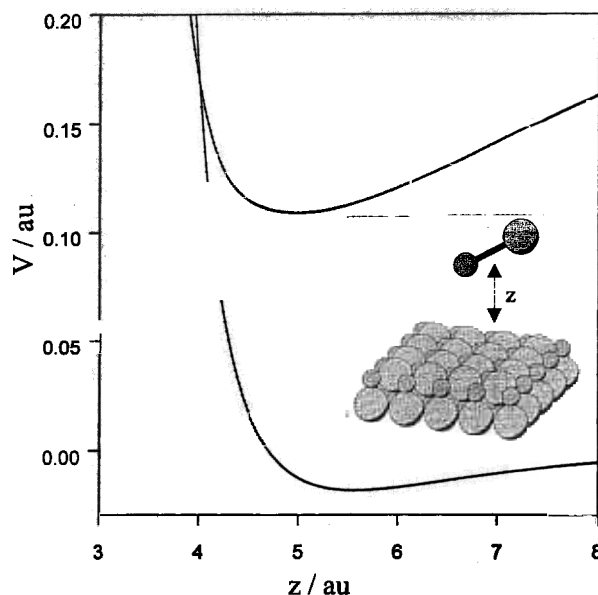


Fig. 1. One-dimensional PES configuration with the vertical shift corresponding to an excitation energy of $\Delta E = 6.4$ eV.

duce the results of near-edge X-ray absorption fine structure (NEXAFS) spectra for the $\text{NO}/\text{NiO}(100)$ -system.¹⁷ An analytical expression of the two-dimensional potential energy surface is given in ref 26. The one-dimensional version is very well represented by the Morse potential

$$V_{gr}(z) = D_e \cdot (1 - \exp(-\alpha \cdot (z - z_0)))^2 - D_e \quad (3)$$

with $D_e = 0.0182$ au, $\alpha = 0.825$ au⁻¹, and $z_0 = 5.56$ au. The dissociation energy matches the experimental value of about 0.5 eV.¹⁷

2.3. Results

The two experimental observables—namely, the desorption probability and the asymptotic velocity distribution of the desorbing species resulting from a one-dimensional treatment—are shown in Figs. 2 and 3 as a function of the resonance lifetime τ . The desorption probability shows the typical saturation at very high resonance lifetimes which are only of theoretical interest. In the case of these large resonance lifetimes within the saturation regime, the computations for the large residence-times mentioned in section 2.1 are needed in order to get converged results. The range of more realistic values is shown enlarged in the inset. From Fig. 2 a resonance lifetime of the excited-state wave packet in the range between 15 fs and 35 fs can be estimated because this range yields desorption probabilities per excitation event between 1% and 10%. This range is consistent with the experimental desorption cross sections measured for oxide systems which are one to four orders of magnitude larger than for typical metal systems.²⁷

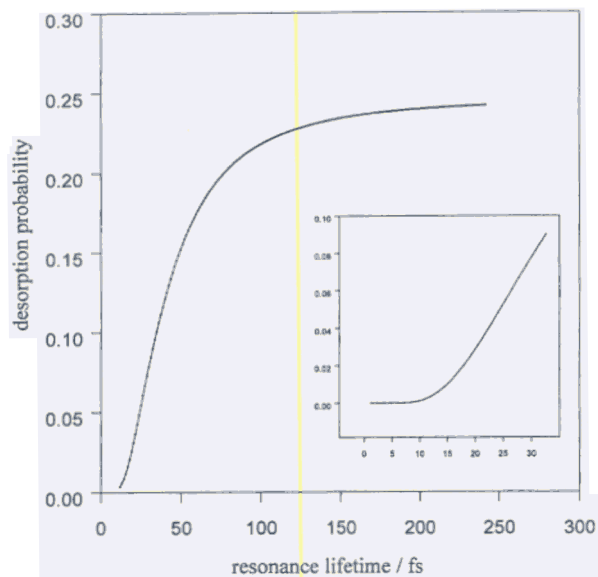


Figure 3 shows k-space probability densities which directly correspond to velocity distributions. These velocity distributions were calculated by separating the asymptotic parts of the wavefunction as described in section 2.1, followed by lifetime-averaging the corresponding k-space probability densities $|\psi_k|^2(t_n)$. The intensities of the distributions shown in Fig. 3 were rescaled to allow for an easy comparison. All of the presented distributions are located within the experimental velocity range of 0–2500 m/s; the maximum of the distributions is slightly shifted towards higher velocities if the resonance lifetime τ increases, especially when considering the difference seen between $\tau = 12$ fs and $\tau = 24$ fs. As expected, the shapes of the velocity distributions do not show any features in this one-dimensional treatment.

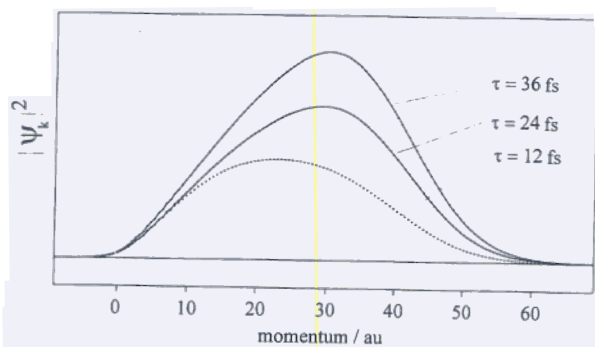


Fig. 3. Lifetime-averaged velocity distributions (50 au = 2000 m/s). The intensities of the three distributions were scaled.

3. TWO-DIMENSIONAL WAVE PACKET CALCULATIONS

The velocity distributions resulting from one-dimensional calculations are monomodal after carrying out the lifetime-averaging procedure, as was shown in the last section. For this reason, the dimension of the wave packet simulations was increased in order to investigate the influence of an angular coordinate, especially with respect to the features of the velocity distributions of the desorbing NO molecules. In the calculations presented in this section, the angle θ between the surface normal and the NO axis is included as a further dimension. The distance coordinate z still accounts for the distance of the center of mass point of the NO molecule from the surface, as indicated in the inset of Fig. 4.

3.1. The Hamiltonian

The Hamiltonian used in the two-dimensional simulations consists of a kinetic energy part $\hat{T}$, which treats the rotation of the NO-molecule like the one of a particle on a ring:

$$\hat{H}(z, \theta) = -\frac{\hbar^2}{2 \cdot M} \cdot \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2 \cdot I} \cdot \frac{\partial^2}{\partial \theta^2} + \hat{V}(z, \theta) \quad (4)$$

with

$$I = \mu \cdot r_e^2 \quad (5)$$

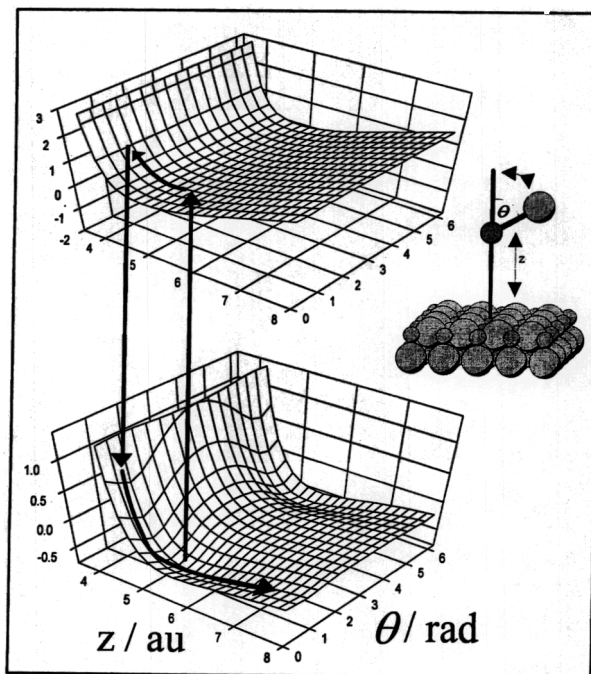


Fig. 4. Two-dimensional PES configuration with an Antoniewicz-like desorption mechanism indicated. The ground-state PES displays two minima of about 0.5 eV, corresponding to two possible 45° configurations.

In eqs 3 and 4 the symbols M , I , μ , and r_e denote the total mass of the NO molecule, the moment of inertia of the NO molecule, the reduced mass of NO, and the equilibrium distance ($r_e = 2.175$ au) within the NO molecule, respectively.

The angle θ is defined on the interval $[0:2\pi]$, allowing for a full rotation of the NO molecule in a plane perpendicular to the surface.

In the two-dimensional approach the two coordinates can be treated separately by means of Fourier transformations to the corresponding momentum representations, where the operation $\hat{T} \cdot \psi$ is evaluated in a straightforward manner.¹⁹ It simply consists of a multiplication of the wavefunction by the kinetic energy spectrum $k_z^2/2 \cdot m$ in the distance coordinate and by the rotational energy spectrum $k_\theta^2/2 \cdot I$ in the angular coordinate.

3.2. Computational Methods and Parameters

The grid parameters with respect to the distance coordinate z do not differ from those mentioned in section 2.1. An equidistant grid in the θ -coordinate was constructed to range from 0 to 2π with a grid spacing of exactly $\Delta k_\theta = 1.0$ au in the angular momentum representation consisting of 64 gridpoints in θ . Transfer function (eq 1) was again used in the distance coordinate to separate the desorbed parts of the wavefunctions.

3.3. The Potentials

In these two-dimensional studies, the charge-transfer-state $V_{CT}(z, \theta)$ was assumed to be angular independent. For this reason, the dependence of the potential energy on the distance coordinate z was assumed to be the one of the 45° geometry (shown in Fig. 1) for all polar angles θ . This assumption is considered as a reasonable first guess and allows for an interpretation of the results presented in the next section in a very straightforward manner.

As discussed above, the angle θ is defined on the interval $[0:2\pi]$. This is the reason for the existence of two minima in the ground-state potential $V_g(z, \theta)$ shown at the bottom of Fig. 4. These two minima with a depth of 0.49 eV correspond to a 45° and 315° geometry, which are equivalent by symmetry. The ground-state potential is characterized by a mirror plane at $\theta = \pi$, the potential energy barrier between the 45° and the 315° geometry is 0.35 eV at the equilibrium distance $z = 5.6$ au. This ground-state potential is a modified version of the potential energy surface used in refs 24–26.

3.4. Results

Before presenting the results of the two-dimensional study, one aspect of the computational procedure has to be clarified at this stage. In order to be able to assign the

one-dimensional velocity distributions with the "particle on a ring" quantum number m , each quantum trajectory is calculated with an initial wave packet once localized in the 45° minimum and once localized in the 315° minimum of the ground-state potential. The distributions resulting from these two starting conditions have to be averaged in order to describe the twofold degeneracy of the rotational levels with the quantum number m correctly. One could get the same result by simple symmetry considerations.

Due to the angular independence of the excited-state potential, the lifetime-weighted total desorption probability as a function of the resonance lifetime τ does not differ significantly from the results of the one-dimensional treatment and is not shown here. This behavior is different from the results presented in another study, where a one-dimensional treatment is compared with a two-dimensional investigation as well.²⁸

Figure 5 shows the lifetime-averaged and angular momentum resolved velocity distributions assigned

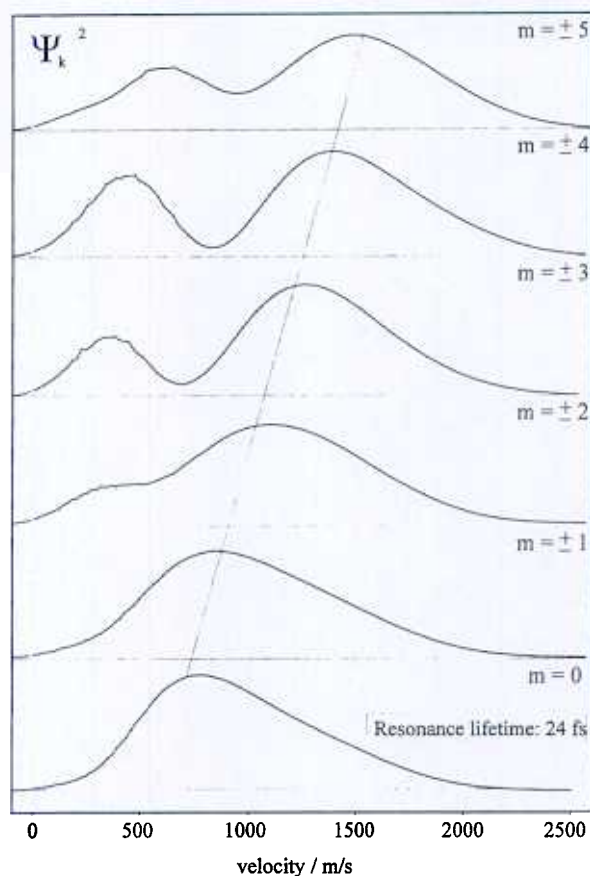


Fig. 5. Lifetime-averaged velocity distributions resulting from the two-dimensional calculations. Shown are the distributions of the first six angular momenta in case of a resonance lifetime $\tau = 24$ fs (1000 au).

with the quantum numbers $m = 0$ up to $m = \pm 5$. A resonance lifetime of $\tau = 1000$ au ($= 24$ fs), which yields a reasonable desorption probability of 5%, was chosen for the averaging procedure. First of all, it is observed that the velocity distributions show significant bimodal features even after a lifetime-averaging procedure. This is certainly a result of the inclusion of an angular coordinate into the wave packet simulations. Furthermore, the experimentally observed shift of the fast channel to higher velocities with increasing rotational excitation in case of a fixed vibrational state¹⁵ occurs in the simulated velocity distributions as well. This coupling of translation and rotation is indicated by the solid line in Fig. 5. Finally, the velocity range of the desorbing species matches the experimental one ranging from 0 m/s to a maximum value of 2500 m/s. These results are encouraging, especially considering the simplicity of the chosen model, but an analysis of the origin of the features within the velocity distributions, for example, is difficult. One reason for this difficulty is the fact that the distributions shown in Fig. 5 are lifetime averaged. A more detailed analysis, which will be published elsewhere, has revealed that different Franck–Condon relaxation regions of the excited state wave packet onto the ground-state potential yield significant features in the asymptotic momentum space distributions.²⁹ For example, in case of a fixed residence-time in the excited state, the resulting bimodal features in the velocity distribution can be resolved by simply dividing the quenched wave packet into two partial wave packets with respect to the angular coordinate.²⁹

Figure 6 emphasizes the importance of the angular dependence of the ground-state potential. In this case both potential energy surfaces were chosen to be angular independent, with the 45° geometry representing the z -dependence of the potential energy for all polar angles. Using the rotational vibrational ground-state wave packet as the initial wavefunction, the resulting velocity distributions are monomodal and do not show any features at all in this case of a fixed residence-time of 72 fs of the wave packet in the excited state. A stochastic lifetime-averaging procedure yields essentially the same results.

In conclusion, the inclusion of the angular coordinate in our calculations is crucial even for a qualitative understanding of the experimental velocity distributions.

4. THE THREE-DIMENSIONAL HAMILTONIAN

The treatment in the former sections is very simplified, because the complete description of the degrees of freedom of a desorbing molecule should include another coordinate, namely the azimuthal angle ϕ . This angle

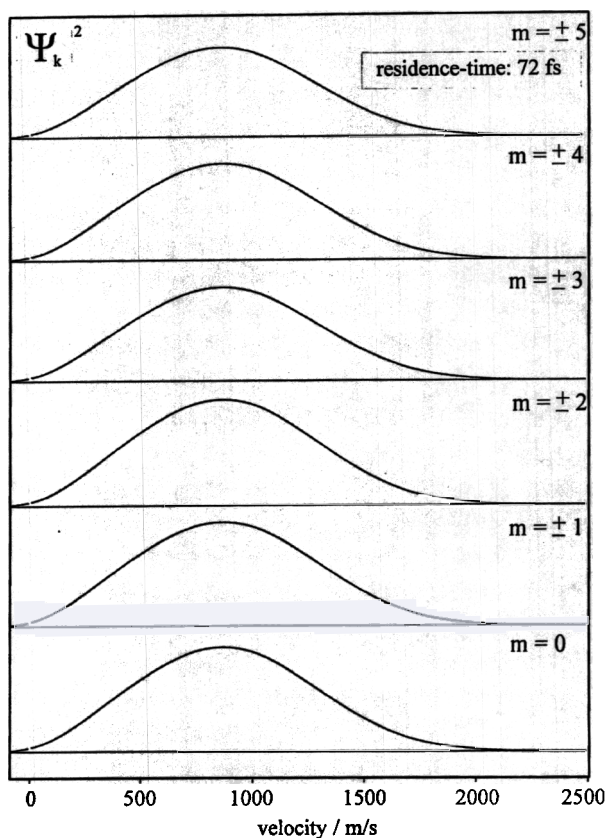


Fig. 6. Velocity distributions for an angular-independent ground-state PES. In this case the distributions of the first six angular momenta are shown for a fixed excited-state residence-time $\tau = 72$ fs (3000 au).

accounts for the rotation of the NO molecule around the surface normal. Efficient methods of solving the time-dependent Schrödinger equation including spherical coordinates are proposed and applied to simulate velocity distributions resulting from a DIET process in a more advanced manner.^{30,12} The angular part of the three-dimensional Hamiltonian

$$\hat{H}(z, \theta, \phi) = -\frac{\hbar^2}{2 \cdot M} \cdot \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2 \cdot I} \times \left(\frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} \cdot \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \cdot \frac{\partial^2}{\partial \phi^2} \right) + \hat{V}(z, \theta, \phi) \quad (6)$$

is mapped on the initial wavefunction after a Gauss–Legendre–Fourier transform between the coordinate and conjugate angular momentum representations. The translational kinetic energy operator is still evaluated by a Fourier transform. By performing high quality ab initio configuration interaction (CI) calculations,¹² a representative charge transfer state in z and θ was constructed. This potential energy surface has been shown to be nearly isotropic in the azimuthal angle ϕ .²³

The final state distributions resulting from the wave

packet calculations with the three-dimensional Hamiltonian (6) using the angular dependent ab initio charge-transfer-state potential¹² are shown in Fig. 7. The lifetime-averaged distributions are calculated for a resonance lifetime of 24 fs (yielding a desorption probability of 3.3%) and are this time assigned by the correct free rotator quantum number l . A very interesting aspect concerns the nuclear dynamics on the ab initio excited state. If the corresponding momentum distributions are observed during the excited state wave packet propagation, clear bimodal features are present after some femtoseconds.¹² These features are caused by the generation of two partial wave packets due to the topology of the ab initio PES and justify the interpretation of the shape of the experimental velocity distributions in terms of a geometric bifurcation on this charge transfer state. In this context, a new mechanistic insight has been gained in the sense that bimodal features in the velocity distributions already arise during the propagation of the wave packet on the excited-state PES. However, the topology of the excited-state PES is a result of a complicated interplay between Coulomb attraction and angular-dependent Pauli-repulsion. A detailed analysis will be presented in a forthcoming paper.

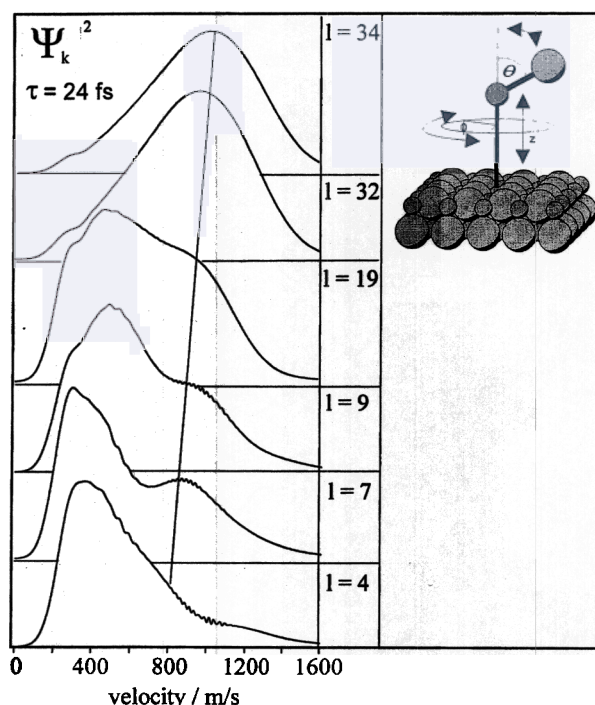


Fig. 7. Lifetime-averaged velocity distributions resulting from wave packet calculations with the three-dimensional Hamiltonian. Shown are the distributions for six arbitrary rotational quantum numbers l . A resonance lifetime of $\tau = 24$ fs (1000 au) was used.

5. SUMMARY

Performing time-dependent quantum-mechanical wave packet simulations, we have investigated the influence of an angular coordinate on the resulting asymptotic velocity distributions of NO desorbing from a NiO(100) surface.

In all cases, reasonable desorption probabilities are calculated if a resonance lifetime of the excited state on the order of 15–35 fs is assumed. This lifetime of the intermediate occurring in laser-induced desorption of a small molecule from an oxide surface seems to be significantly larger than in the case of systems where metals are involved.

In the one-dimensional treatment the asymptotic velocity distributions are monomodal, as is obvious and expected.

Including the polar angle between the NO axis and the surface normal yields bimodal velocity distributions in the experimental velocity range even after a lifetime-averaging procedure. In this part of the study the bimodality in the velocity distributions has been traced back to the angular dependence of the ground-state potential as a reason for this phenomenon.

However, including formally also the azimuth angle ϕ accounts for the most realistic and advanced description of the DIET process. In this approach the reason for this bimodality of the velocity distributions, which is observed in experiment, has been shown previously to be due to the topology of a representative charge transfer state which takes part in the desorption process and which has been calculated on an ab initio basis. The bimodality in the final state distributions occurs within this argumentation because the wave packet bifurcates on the charge transfer state where it has been transferred by the exciting laser. Therefore, bimodality turns out to be a feature that already occurs when a wave packet propagates on the excited state PES. This new aspect would not have been found without having considered a non-empirical excited-state potential energy surface.

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REFERENCES AND NOTES

- (1) Menzel, D.; Gomer, R. *J. Chem. Phys.* **1964**, *41*, 3311–3328.
- (2) Redhead, P.A. *Can. J. Phys.* **1964**, *42*, 886–905.
- (3) Klüner, T.; Freund, H.-J.; Freitag, J.; Staemmler, V. *J. Chem. Phys.* **1996**, *104*, 10030–10040.

- (4) Antoniewicz, P.R. *Phys. Rev. B* **1980**, 21, 3811–3815.
- (5) Burns, A.R.; Stechel, E.B.; Jennison, D.R.; Li, Y.S. *J. Chem. Phys.* **1994**, 101, 6318–6329.
- (6) Saalfrank, P. *Surf. Sci.* **1997**, 390, 1–10.
- (7) Balakrishnan, N.; Kalyanaraman, C.; Sathyamurthy, N. *Phys. Rep.* **1997**, 280, 79–144.
- (8) Gortel, Z.W.; Wierzbicki, A. *Phys. Rev. B* **1991**, 43, 7487–7501.
- (9) Gou, H.; Seideman, T. *J. Chem. Phys.* **1995**, 103, 9062–9073.
- (10) Harris, S.; Holloway, S.; Darling, G.R. *J. Chem. Phys.* **1995**, 102, 8235–8248.
- (11) Zimmermann, F.; Ho, W. *Surf. Sci. Rep.* **1995**, 22, 127–247.
- (12) Klüner, T.; Freund, H.-J.; Staemmler, V.; Kosloff, R. *Phys. Rev. Lett.* **1998**, 80, 5208–5211.
- (13) Hasselbrink, E.; Wolf, M.; Holloway, S.; Saalfrank, P. *Surf. Sci.* **1996**, 363, 179–184.
- (14) Klüner, T.; Thiel, S.; Freund, H.-J.; Staemmler, V. *Chem. Phys. Lett.* **1998**, 294, 413–418.
- (15) Mull, T.; Baumeister, B.; Menges, M.; Freund, H.-J.; Weide, D.; Fischer, C.; Andresen, P. *J. Chem. Phys.* **1992**, 96, 7108–7116.
- (16) Eichhorn, G.; Richter, M.; Al-Shamery, K.; Zacharias, H. *Surf. Sci.* **1996**, 368, 67–70.
- (17) Kühlenbeck, H.; Odörfer, G.; Jaeger, R.; Illing, G.; Menges, M.; Mull, T.; Freund, H.-J.; Pöhlchen, M.; Staemmler, V.; Witzel, S.; Scharfschwerdt, C.; Wennemann, K.; Liedtke, T.; Neumann, M. *Phys. Rev. B* **1991**, 43, 1969–1986.
- (18) Heather, R.; Metiu, H. *J. Chem. Phys.* **1987**, 86, 5009–5017.
- (19) Kosloff, R. *J. Phys. Chem.* **1988**, 92, 2087–2100.
- (20) Kosloff, R.; Tal-Ezer, H. *Chem. Phys. Lett.* **1986**, 127, 223–230.
- (21) Gadzuk, J.W.; Richter, L.J.; Buntin, S.A.; King, S.A.; Cavanagh, R.R. *Surf. Sci.* **1990**, 235, 317–333.
- (22) Gadzuk, J.W. *Surf. Sci.* **1995**, 342, 345–358.
- (23) Klüner, T.; Freund, H.-J.; Freitag, J.; Staemmler, V.; J. *Mol. Catal. A* **1997**, 119, 155–163.
- (24) Smedley, J.E.; Corey, G.C.; Alexander, M.H. *J. Chem. Phys.* **1987**, 87, 3218–3231.
- (25) Muhlhausen, C.W.; Williams, L.R.; Tully, J.C. *J. Chem. Phys.* **1985**, 83, 2594–2606.
- (26) Baumeister, B. Ph.D. Thesis. Ruhr-Universität Bochum, **1994**.
- (27) Menges, M.; Baumeister, B.; Al-Shamery, K.; Freund, H.-J.; Fischer, C.; Andresen, P. *J. Chem. Phys.* **1994**, 101, 3318–3325.
- (28) Finger, K.; Saalfrank, P. *Chem. Phys. Lett.* **1997**, 268, 291–299.
- (29) Klüner, T.; Thiel, S.; Freund, H.-J.; Staemmler, V.; Kosloff, R. Submitted to *J. Chem. Phys.*
- (30) Corey, G.C.; Lemoine, D. *J. Chem. Phys.* **1992**, 97, 4115–4126.