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Citation: J. Chem. Phys. 137, 064705 (2012); doi: 10.1063/1.4738596
View online: http://dx.doi.org/10.1063/1.4738596
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Published by the American Institute of Physics.

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On the determination of absolute vibrational excitation probabilities in molecule-surface scattering: Case study of NO on Au(111)

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(Received 29 April 2012; accepted 5 July 2012; published online 10 August 2012)

We describe a method to obtain absolute vibrational excitation probabilities of molecules scattering from a surface based on measurements of the rotational state, scattering angle, and temporal distributions of the scattered molecules and apply this method to the vibrational excitation of NO scattering from Au(111). We report the absolute excitation probabilities to the \( v = 1 \) and \( v = 2 \) vibrational states, rotational excitation distributions, and final scattering angle distributions for a wide range of incidence energies and surface temperatures. In addition to demonstrating the methodology for obtaining absolute scattering probabilities, these results provide an excellent benchmark for theoretical calculations of molecule-surface scattering.

I. INTRODUCTION

A fundamental molecular level insight into the underlying dynamics of energy exchange between molecules and metal surfaces is a vital prerequisite to a comprehensive theory of gas-surface chemistry, bearing on subjects ranging from corrosion and electrochemistry to heterogeneous catalysis. The experimental evidence accumulated over more than two decades\(^1\)–\(^18\) accompanied by powerful theoretical analysis\(^19\)–\(^27\) leave little doubt as to the existence of electronically nonadiabatic influences–Born-Oppenheimer approximation breakdown–on these energy transfer processes. Energy transfer between electron-hole pairs (EHP) in the metal and vibrational degrees of freedom (EHP-V) has received particular attention,\(^3\)–\(^5\),\(^9\)–\(^12\),\(^20\)–\(^22\),\(^24\)–\(^26\) as vibration is a degree of freedom coupling directly to the reaction coordinate.

Molecular beam-surface scattering experiments combined with laser based methods of preparation and detection enable control over orientation, velocity, and the internal state of the gaseous collision partner, and hence produce experimental results that can be directly compared to high-level theoretical calculations. The ample evidence of energy exchange between molecular vibrations and metallic EHPs gained from molecular beam-surface scattering experiments includes studies of (single and multi-quantum) vibrational excitation,\(^8\)–\(^12\),\(^28\) (single and multi-quantum) vibrational relaxation,\(^4\),\(^22\) and electron emission\(^8\),\(^16\),\(^19\) occurring in the course of molecule-surface encounters. Specifically, vibrational excitation exhibiting an Arrhenius-like surface temperature dependence with activation energy equal to the vibrational excitation energy is often considered to be a signature of electronically nonadiabatic behavior in molecule-surface encounters.\(^7\),\(^10\),\(^12\)

While the surface temperature dependence of vibrational excitation has been investigated in detail,\(^10\),\(^12\) the absolute values of vibrational excitation probability and the magnitude of the pre-exponent in Arrhenius surface temperature dependence received little attention until recently.\(^7\)–\(^9\) Disregarding the absolute values of vibrational excitation probability and focusing entirely on the temperature dependence is unfortunate since the magnitude of the pre-exponential coefficient provides information about the strength of electronically nonadiabatic coupling for a given molecule-surface system.\(^1\),\(^7\) Very recently absolute vibrational excitation probabilities were reported for single and multi-quantum vibrational excitation of NO scattered from Au(111) (Ref. 9) and a state-to-state kinetic model was used to analyze and interpret the pre-exponential factors in Arrhenius-like surface temperature dependence and compare the intrinsic likelihood of EHP-V coupling for different EHP-mediated vibrational excitation events.\(^1\),\(^7\) Furthermore, experiments examining the absolute probability of vibrational excitation provide a stringent test for the theories of electronically nonadiabatic interactions. The comparison of extensive absolute vibrational excitation probability data to predictions of perturbative electronic friction theory\(^22\),\(^24\) and to independent electron surface hopping (IESH) theory\(^19\) leaves little doubt that EHP-V coupling occurs via formation of transient negative ions.\(^30\)

Clearly, accurate measurement of absolute vibrational excitation probabilities over a wide range of incidence translational energies and surface temperatures is a mandatory prerequisite for such in-depth understanding of the EHP-V coupling mechanism. Measuring absolute excitation probabilities is a difficult task that requires various experimental techniques.
factors to be taken into consideration: detector response, choice of a spectral band, knowledge of transition strengths, laser pulse energy dependence of the signal, angular and temporal distributions of the scattered molecules, velocity of the scattered molecules, etc. In this work, we provide a detailed account of how these factors should be taken into consideration in evaluating absolute vibrational excitation probabilities by considering the case of NO colliding with Au(111) surface.

Specifically, the experimental protocol presented in this work is employed to determine absolute vibrational excitation probabilities for both the fundamental, NO(v = 0 → 1), and first overtone transition, NO(v = 0 → 2), when NO is scattered from a Au(111) surface at six different incidence energies, Ei, from 0.11 eV to 1.05 eV at surface temperatures, Tg, ranging from 300 K to 1000 K. These results provide an extensive benchmark dataset that probes the EHP-V coupling for this system suitable for comparison with theories of electronically nonadiabatic interactions in molecule surface collisions. Furthermore, the experimental protocol described here should be applicable to the measurement of absolute transition probabilities for other systems.

II. EXPERIMENTAL METHODS

Our gas-surface scattering apparatus has been described previously in detail. Supersonic molecular beams of NO are produced using a 10-Hz piezo-electrically driven pulsed valve. The translational energy distribution of the beams is adjusted by seeding NO in inert carrier gases with varying mass.

See Table I. The beam is skimmed, passes through two stages of differential pumping, and subsequently enters an ultra-high vacuum scattering chamber where the NO molecules scatter from a Au(111) crystal at near normal incidence. A schematic of the machine is presented in Fig. 1. The Au(111) surface temperature can be varied, from room temperature to the melting point of the crystal, by resistive heating of tungsten wires. The scattering chamber has a base pressure of $\sim 1.5 \times 10^{-10}$ Torr, increasing to $\sim 1 \times 10^{-9}$ Torr with the molecular beam running. The Au(111) surface was cleaned by argon ion bombardment, for $\sim 1$ h, checked for contamination with Auger spectroscopy, and annealed for $\sim 45$ min prior to scattering experiments. The sample is then cooled to room temperature before beginning scattering experiments. After scattering experiments, the surface was again checked for contamination using Auger spectroscopy, with no major contamination found. The scattering chamber is equipped with optical ports allowing the use of UV ($\sim 230$ nm) and IR ($\sim 1.8$ $\mu$m) laser beams, which are generated with Q-switched Nd:YAG-pumped dye lasers with appropriate frequency conversion schemes. The UV radiation is used for quantum state selective (1+1) REMPI ionization of scattered NO via $\Delta^2 \Sigma^+ (v') \rightarrow \Sigma^2 \Pi(v'')$ transitions, known as the $\gamma_{v',v''}$-bands. The ions are collected with ion optics (two-element cylindrical ion lens and repeller) and detected by a dual micro-channel plate detector (MCP).

In many experiments, there was a high ion background associated with heating the crystal. We believe this background stems from emission of $K^+$ ions from the W wires used to heat the Au(111) sample. The background was so high that it reduced the gain of the MCP detector. Since the background was CW, and the signal was pulsed, we pulsed the MCP so that it was only on during the time the signal was present. This reduced the gain depletion problem to acceptable levels. The magnitude of the voltage across the MCP was adjusted for each vibrational state such that the signal intensity was not saturated. To calibrate the relative MCP gain, the variation of a small ion signal was measured over the entire range of the MCP voltages used in this work, where the strength of the signal was chosen to avoid saturation at the highest gain (see Sec. III).

To accurately determine the absolute vibrational excitation probabilities (as elaborated in detail in Sec. III), spectral, angular (spatial), and temporal distributions of incident and scattered NO molecules must be recorded. By scanning the wavelength of the REMPI laser over the $\Delta^2 \Sigma^+ (v' = 0) \rightarrow \Sigma^2 \Pi(v'' = 0,1,2)$ vibrational bands, rotationally resolved spectra of NO($v = 0,1,2$) in the incident and scattered beam were recorded (see Sec. III B). The angular distributions

![Fig. 1. Schematic of the experimental apparatus. The molecules leave the pulsed valve (PV) and pass through a skimmer (Sk). The incident molecular beam (I) strikes a Au(111) surface at nearly normal incidence. The scattered molecules (S) are ionized with a laser (black circle). The ions are directed via a repeller (R) and an ion lens (L) to a microchannel (MCP) plate array where they are detected. The detection laser can be translated parallel to the surface ($\sim 22$ mm) as represented by the thin dashed line.](image-url)
of the scattered and incident beams were recorded by vertical translation of the REMPI laser beam in the plane perpendicular to the molecular beam (see Sec. III C). The temporal distribution of the scattered and incident beams was measured by recording the REMPI signal at a variety of delays between the opening of the pulsed nozzle and firing of the REMPI laser (see Sec. III D).

To quantify the degree of translational inelasticity and the translation-vibration (T-V) coupling required for flux-density corrections, accurate high resolution measurements of incident and scattered velocity distributions are required. IR-UV double resonance is used for accurate velocity measurements of the molecular beams.32,33 The velocities of the incident and scattered molecules were obtained from the analysis of time-of-flight spectra measured by state-specific ionization of NO tagged via vibrational overtone pumping by an IR laser a known distance from the UV laser beam used for REMPI detection.

III. RESULTS

A. Overview of experimental principles

In this work, we report absolute vibrational excitation probabilities, \( P_{0-v} \), for NO(0 \( \rightarrow \) v) transitions resulting from collisions with the (111) surface of solid gold. Below we describe the derivation of \( P_{0-v} \) from laboratory observations of REMPI signal strengths. For the conditions of single-bounce direct scattering, \( P_{0-v} \) is defined as the ratio of scattered molecules in state v to all scattered molecules

\[
P_{0-v} = \frac{N_v}{\sum N_v}.
\]

For the case where almost all NO molecules are initially in v = 0 and when the sum of the vibrational excitation probabilities is much less than unity, as in this work, Eq. (1) can be simplified as follows:

\[
P_{0-v} \approx \frac{N_v}{N_0} = \frac{\text{Number of scattered molecules in state } v}{\text{Number of scattered molecules in } v = 0}.
\]

Thus, by determining the ratio of \( N_v \) to \( N_0 \), we obtain absolute vibrational excitation probabilities.

The practical requirements for implementing this conceptually simple strategy are, however, rather complicated. Specifically, we require vibrational state specific information on scattered molecules, such as scattering angular, \( \Theta_v(\theta_v) \), and rotational population, \( n_v(j) \), distributions. Here, \( \theta_v \) represents the scattering angle with respect to the surface normal, \( j \) represents the rotational quantum numbers of the scattered molecules in vibrational state v probed by the (1+1) REMPI detection scheme. In general, one also needs rotational line strengths, \( S(j_\Sigma, j) \), and Franck-Condon factors, \( Q(v_\Sigma, v) \), for the resonant \( A^2 \Sigma^+ \rightarrow \pi^2 \Pi(v') \) transition of NO. Here, \( j_\Sigma \) and \( v_\Sigma \) represent the rotational and vibrational quantum numbers, respectively, of the intermediate, electronically excited \( A^2 \Sigma^+ \) state used in the (1+1) REMPI scheme. We must also consider the wavelength dependent ionization cross section of the intermediate, electronically excited \( A^2 \Sigma^+ \) state, \( \sigma_{v_\Sigma}(\lambda_{\text{MPI}}) \), where \( \lambda_{\text{MPI}} \) is the laser wavelength used to detect state v via state v\textsubscript{2} by REMPI. The REMPI signal also depends on the time delay, \( \tau \), between the opening of the pulsed nozzle and firing of the pulsed detection laser. This is described by a time dependent function, \( \Delta_v(\tau) \). This function may be different for each vibrational channel as the average velocity, \( \langle u_v \rangle \), of the scattered molecules depends on the final vibrational state. The time delay between opening of the pulsed nozzle and firing the detection laser, \( \tau_v \), and the angle with respect to the surface normal, \( \theta_v \), may be chosen differently for each v-state probed, for reasons of convenience, as will be explained in Secs. III B–III F. Table II provides an overview of the functions and variables given in this section.

Noting that REMPI signals are proportional to molecular density, are a function of the laser pulse energy, \( f(I_v) \), and the MCP gain, \( \Gamma_v \), we arrive at a relationship between REMPI signal strength, \( \text{SIG}(j_\Sigma, j, \theta_v, \tau_v) \), and \( n_v(j) \), shown below

\[
\text{SIG}(j_\Sigma, j, \theta_v, \tau_v) \propto \frac{n_v(j)}{\langle u_v \rangle} \times S(j_\Sigma, j) \times \Theta_v(\theta_v) \times Q(v_\Sigma, v) \times \sigma_{v_\Sigma}(\lambda_{\text{MPI}}) \times \Delta_v(\tau_v) \times \Gamma_v \times f(I_v).
\]

Here, dividing by the average velocity of the scattered molecules, \( \langle u_v \rangle \), is used for the density-to-flux conversion.34 \( \theta_v \) and \( \tau_v \) are chosen to maximize the signal and minimize background, such as signal arising from the incident beam.

We can invert Eq. (3) as follows:

\[
n_v(j) \propto \frac{\text{SIG}(j_\Sigma, j, \theta_v, \tau_v) \times \langle u_v \rangle}{S(j_\Sigma, j) \times \Theta_v(\theta_v) \times Q(v_\Sigma, v) \times \sigma_{v_\Sigma}(\lambda_{\text{MPI}}) \times \Delta_v(\tau_v) \times \Gamma_v \times f(I_v)}.
\]
To obtain $N_v$, we must sum over the populations of all rotational states, $j$,

$$
N_v = \sum_j n_s(j) \propto \sum_j \frac{\text{SIG}_v(j, j, \theta_v, \tau_v) \times \langle u_\nu \rangle}{S(j_j, j) \times \Theta_v(\theta_v) \times Q(v_j, v) \times \sigma_v(\lambda_{\text{MPI}, v}) \times \Delta_v(\tau_v) \times \Gamma_v \times f(I_v)}.
$$

(5)

Plugging this result back into Eq. (2) yields the following:

$$
P_{0\sim v} \approx \frac{N_v}{N_0} = \frac{\sum_j \frac{\text{SIG}_v(j, j, \theta_v, \tau_v) \times \langle u_\nu \rangle}{S(j_j, j) \times \Theta_v(\theta_v) \times Q(v_j, v) \times \sigma_v(\lambda_{\text{MPI}, v}) \times \Delta_v(\tau_v) \times \Gamma_v \times f(I_v)}}{\sum_j \frac{\text{SIG}_0(j, j, \theta_0, \tau_0) \times \langle u_0 \rangle}{S(j_j, j) \times \Theta_0(\theta_0) \times Q(v_j, 0) \times \sigma_v(\lambda_{\text{MPI}, 0}) \times \Delta_0(\tau_0) \times \Gamma_0 \times f(I_0)}}.
$$

(6)

This expression can be simplified, since under our experimental conditions the first (resonant) step in the (1+1) REMPI scheme is saturated. Saturation means that the signal is independent of the rotational line strengths, $S(j_j, j)$, and Franck-Condon factors, $Q(v_j, v)$. The saturation of the resonant step in the (1+1) REMPI scheme is discussed in Sec. III E in relation to the laser pulse energy dependence. This leads to the key expression used to derive absolute vibrational excitation probabilities

$$
P_{0\sim v} \approx \frac{N_v}{N_0} = \left(\frac{\sum_j \text{SIG}_v(j, j, \theta_v, \tau_v)}{\sum_j \text{SIG}_0(j, j, \theta_0, \tau_0)}\right) \times \frac{\langle u_\nu \rangle \times \Theta_v(\theta_v) \times \sigma_v(\lambda_{\text{MPI}, v}) \times \Delta_v(\tau_v) \times \Gamma_v \times f(I_v)}{\langle u_0 \rangle \times \Theta_0(\theta_0) \times \sigma_v(\lambda_{\text{MPI}, 0}) \times \Delta_0(\tau_0) \times \Gamma_0 \times f(I_0)}.
$$

(7)

In Secs. III B–III F, we describe the practical implementation of the above described approach. Briefly, we carry out measurements of $\sum_j \text{SIG}_v(j, j, \theta_v, \tau_v)$ by conducting laser scans over an entire vibronic band at chosen values of $\theta_v$, $\tau_v$, $\Gamma_v$, and $I_v$ and then integrating the signal intensity over the entire band. Rotationally resolved REMPI spectra are recorded via spectrally well-isolated bands, which determine $\lambda_{\text{MPI}}$. We adjust $\Gamma_v$ to avoid MCP saturation and $I_v$ to ensure saturation of the resonant step in the REMPI scheme. In separate but similar experiments, we measure $\sum_j \text{SIG}_0(j, j, \theta_0, \tau_0)$, choosing $\theta_0$, $\tau_0$, $\Gamma_0$, and $I_0$ based on similar considerations. In the absence of trapping and for the case where $N_v \ll N_0$, $N_0$ is nearly independent of surface temperature, which we verified. Thus, for each incidence energy of translation, a single value of $N_0$ measured at $T_s = 300$ K is used to derive $P_{0\sim v}$ for different surface temperatures. We also carry out measurements of angular distributions, $\Theta_v$ and $\Theta_0$, and time delay distributions, $\Delta_v$ and $\Delta_0$, to account for the specific scattering angle and delay time $\theta_v$ and $\tau_v$, chosen for the measurement of the signal $\text{SIG}_v(j, j, \theta_v, \tau_v)$. We used literature values of ionization

![Image](https://example.com/image.png)
cross sections \(\sigma_{\text{E}}(\lambda_{\text{MPT}})\). The laser pulse energy dependence of the REMPI signal is measured and fit to a suitable empirical function. We also experimentally characterize the dependence of the signal on the voltage across the MCP detector. With such data in hand, we generate a single value of \(P_{\text{MCP}}\) at a specific choice of \(v\), incidence energy of translation, \(E_i\), and surface temperature, \(T_s\). This procedure was repeated more than 140 times for different values of \(E_i\), \(T_s\) for NO\((v = 0 \rightarrow 1)\), and NO\((v = 0 \rightarrow 2)\).

**B. Primary observations: REMPI scans of isolated vibronic bands, \(\sum_j \sigma_{\text{I}}(j, \theta, \tau)\)**

For each incidence energy listed in Table I, \((1+1)\) REMPI spectra probing NO\((v = 0, 1, 2)\) were recorded at surface temperatures between \(T_s = 300\) and 1000 K. Typical REMPI spectra are shown in Fig. 2. The area under the entire REMPI spectrum is obtained by numerical integration providing the spectral intensity, \(\sum_j \sigma_{\text{I}}(j, \theta, \tau)\), for each vibrational state. Integration over the entire band is advantageous as individual rotational line strength factors and knowledge of the variation of rotational temperature with the surface temperature are not required. At each value of \(E_i\), REMPI spectra such as those of Fig. 2 are measured at several values of \(T_s\). We compare the measurements of the vibrationally excited molecules at various surface temperatures to NO\((v = 0)\) spectra taken at \(T_s = 300\) K. Comparison to a single NO\((v = 0)\) measurement helps minimize the random error in the measurement.

An estimate of the vibrational excitation probability can already be drawn by inspection of the intensity of the REMPI spectra shown in Fig. 2, which have only been corrected for differences in MCP gain and laser pulse energy. These corrections are experimentally measured and described in more detail in Sec. III E. We find that the integrated REMPI signal of NO in its ground vibrational state, \(\sum_j \sigma_{\text{I}}(j, \theta_0, \tau_0)\), is \(\sim 200\)-fold larger than that of NO\((v = 1)\), \(\sum_j \sigma_{\text{I}}(j, \theta_1, \tau_1)\), which is, in turn, \(\sim 25\)-fold larger than that originating from NO\((v = 2)\), \(\sum_j \sigma_{\text{I}}(j, \theta_2, \tau_2)\). These numbers agree with the real excitation probabilities within about a factor of two, indicating that the MCP gain and the laser power are the dominant correction factors for quantitative determination of the absolute excitation.

The NO molecules are probed via the \(\gamma_{0v}\) bands, which are well isolated from other bands of the \(\gamma\)-system and REMPI transitions through other intermediate electronic states. The \(\gamma_{02}\) band is a good example of the bands used in this work. Consider that the nearest overlapping band is \(\gamma_{13}\), which probes NO\((v = 3)\). Overlapping lines from this band are much weaker as NO\((v = 3)\) is much less populated than NO\((v = 2)\). This is demonstrated in Fig. 3. Note that all of the observed lines can be assigned to the \(\gamma_{02}\) band, even those in the inset, where the band-head of \(\gamma_{13}\) is found. This shows that spectral overlap with other bands is avoided and a simple integration over the entire REMPI spectrum yields, in this case, \(\sum_j \sigma_{\text{I}}(j, \theta, \tau)\). For NO\((v = 0 \rightarrow 1)\), a small background was observed which arises from rotationally inelastic, vibrationally elastic scattering of thermally populated NO\((v = 1)\) present in the incident molecular beam. This small contribution to the signal was determined by extrapolating the surface temperature dependence of the NO\((v = 1)\) signal to \(T_s = 0\) K using a suitable Arrhenius expression, and then subtracted.

The rotationally resolved REMPI spectra recorded in the course of absolute excitation probability measurements carry much more information than just the integrated signal. These rotational spectra, examples of which are shown in Fig. 2, have been fit, using LIFBase, to extract a rotational temperature which characterizes the rotational population distributions. Derived rotational temperatures as a function of surface temperature and incidence energy are
shown in Fig. 4. While there is no reason to expect a thermal rotational distribution, a rotational temperature allows a simple and sensible way to compare the extent of rotational excitation of the molecules upon scattering from the surface.

The rotational temperature of the scattered molecules does not depend strongly on the final vibrational state and the surface temperature. The rotational excitation increases when surface temperature or incidence energy is increased. The rotational temperature, except by coincidence, is different than the temperature of the surface, indicating a direct scattering mechanism. These trends in rotational excitation are qualitatively similar to NO scattering from Ag(111).11

C. Primary observations: Angular distributions, $\Theta_v(\theta_e)$

The angular distributions of scattered molecules are, in principle, dependent upon $T_S$, $E_i$, and $v$. Broader angular distributions result in smaller REMPI signals for the same amount of scattered molecules due to spatial dilution. The $(1+1)$ REMPI used in this work employs an unfocused laser, meaning the detection volume is cylindrical with the long axis along the laser propagation direction. This implies that the flux of molecules is linearly proportional to the measured angular distribution, $\Theta_v(\theta_e)$. For narrow angular distributions characteristic of direct scattering, the difference in the resulting signals obtained using a point or a cylindrical detection volume is small. However, as the angular distribution broadens, the difference becomes larger. For example, for the case of the molecules departing the surface by thermal desorption, which exhibits a $\cos\theta$ angular distribution, the angular distribution recorded along the cylindrical detection region appears with a $\cos^2\theta$ dependence, since the measured signal is proportional to the scattered molecular density integrated along the line of sight of the REMPI laser.

Angular distributions of the scattered vibrationally excited molecules were measured for each incidence translational energy described in Sec. II for at least three surface temperatures. These were measured by tuning the laser wavelength to a single REMPI transition and linearly translating the laser parallel to the surface. While ideally the measurement of angular distributions would be measured in a circular arc around the scattering center, for narrow angular distributions the deviations between angular distributions by translating the laser in a circular arc and those measured by translating the laser beam parallel to the surface are negligible. Hence, in this work the correction for these deviations was not required, especially in the view of the fact that scattered angular distributions did not vary significantly for different experimental conditions. For convenience $\theta_0$ was measured at $T_S = 300$ K. REMPI spectra of scattered molecules were typically recorded off the peak of the angular distribution to avoid the spatial overlap of the probe laser with the incident (nearly normal to the surface) molecular beam. The angular distributions observed for the NO/Au(111) system, although narrow, are generally broader than those previously measured for the HCl/Au(111) system using a similar experimental setup.59 For HCl, translational energy couples strongly to vibration.8,32 The scattered vibrationally excited molecules only have enough translational energy to escape the surface at scattering angles near the surface normal. However, for NO the translation to vibration coupling is very weak40 allowing for a broader final angular distribution of scattered molecules.

The angular distributions peak at the specular angle and are much narrower than a $\cos^2\theta$ distribution, which would characterize the molecules undergoing trapping desorption with no dependence of the trapping probability on incidence angle. This result is consistent with the rotational temperature dependencies described above, also indicating direct sub-ps single bounce scattering dynamics.

Each measured angular distribution was fitted to a normalized Gaussian function

$$\Theta_v(\theta) = \frac{\exp\left(-\frac{(\frac{\theta}{\sigma})^2}{2}\right)}{\sqrt{2\pi}\sigma}.$$  (8)

Here, $\theta_0$ is the scattering angle of peak intensity and $\sigma$ is the width parameter of the angular distribution related to the full width at half maximum ($\text{FWHM} = 2\sigma\sqrt{2\ln 2}$). Values of $\sigma$ determined from these fits are given in Appendix A. We used linear interpolation of the width parameter, $\sigma$, to characterize angular distributions at temperatures where measurements were not carried out, since the measured $\theta_0$'s vary only slightly within the range of temperatures used in this work, as shown in Fig. 5. Figure 6 shows the variation in the width parameters with incidence energy. Data are shown for scattered $v = 0$ and $T_S = 300$ K and for $v = 1$ and $v = 2$ at $T_S = 1000$ K. The width decreases slightly with increasing $E_i$. The width of the distribution increases slightly with increasing surface temperature as shown in Fig. 5 and Appendix A.

D. Primary observations: Delay time profiles, $\Delta_v(\tau)$

The delay time profiles, $\Delta_v(\tau)$, are utilized in a similar way as the angular distributions. $\Delta_v(\tau)$ is normalized and can

FIG. 5. Angular distributions are weakly dependent on $T_S$. Angular distributions of NO molecules that underwent the $v = 0 \rightarrow 1$ transition at two surface temperatures filled circles with $T_S = 353$ K and empty circles with $T_S = 973$ K at $E_i = 0.93$ eV. Gaussian fits to the two angular distributions are shown as black curves. The dashed line shows a $\cos^2(\theta)$ function for comparison.
be used to account for differences in the temporal widths of the delay time profiles and for differences in the specific value of $\tau$, at which the experiment was conducted. The delay scan profiles, $\Delta_{\nu}(\tau)$, depend very weakly on the final vibrational state, as shown in the left panel of Fig. 7. There is a surface temperature influence, albeit also weak, on $\Delta_{\nu}(\tau)$, shown in the right panel of Fig. 7 for $\Delta_{1}(\tau)$.

**E. Primary observations: Laser pulse energy dependence, A-state ionization cross sections and MCP gain**

The magnitude of the REMPI signals depends strongly on the laser pulse energy, which is taken into account by normalizing the recorded REMPI signal with an empirical function, $f(I_v)$, derived by fitting the measured power dependence. At low pulse energies neither step of the two-photon absorption process is saturated, resulting in a quadratic dependence of the REMPI signal on the laser pulse energy. At intermediate energies the resonant first photon absorption becomes saturated, leading to a linear laser pulse energy dependence. At sufficiently high pulse energies both absorption steps become saturated, resulting in laser-power independent REMPI signal

$$f(I_v) \propto \begin{cases} I_v^2 & \text{(at low pulse energy)} \\ I_v & \text{(at intermediate pulse energy)} \\ \text{constant} & \text{(at high pulse energy)} \end{cases}$$

(9)

For $(1+1)$ REMPI used in this work, the laser was unfocused with a width of 2 mm, we observe a quadratic dependence below a pulse energy of 0.4 mJ, which becomes linear above $\sim 1$ mJ.

We do not observe the two-photon saturated behavior under our conditions. The reason for this becomes apparent when employing a two-color $(1+1')$ REMPI approach. Here, a 2 mm diameter beam of $\sim 235$ nm light from the doubled output of the tunable dye laser, with a pulse energy between 0.1 and 2 mJ was tuned onto a resonance of the $\gamma$-band and was coaxially overlapped with a 2 mm beam of the Nd:YAG laser’s 4th harmonic at 266 nm with a constant pulse energy of 24 mJ. Under these conditions, NO is resonantly excited to the $A^2\Sigma^+$ state by the output of the low intensity pulse at $\sim 235$ nm and the $A^2\Sigma^+$ state is ionized by both the 230 nm and 266 nm light. Since the ionization cross sections for 235 nm and 266 nm are thought to be similar, the ionization is dominated by the more intense 266 nm pulse and approximately independent of the intensity of the $\sim 230$ nm light. Figure 8 shows the dependence of this $(1+1')$ signal on the energy of the 235 nm pulse for the $\gamma_{01}$ band. One can clearly see the saturation of the resonant step of the $\gamma$ band at a pulse energy of about 1 mJ. In contrast, even with 24 mJ/pulse at 266 nm, the ionization step is not saturated.

For one-color REMPI, laser pulse energy dependencies, $f(I_v)$, were measured for different bands probing scattered NO(0, 1 and 2) as well as NO(v = 0) prepared by leaking NO into the chamber. The results of these measurements, Fig. 9, are interesting to compare to those of Fig. 8. As expected one sees a quadratic intensity dependence at the lowest energies which becomes linear above a laser pulse energy of 1 mJ showing that the second step is not saturated. We find that the laser intensity dependence can be approximated reasonably well by an empirical function $f(I_v) \propto I_v^{1.66}$ over the entire laser intensity range used in this work, independent of vibrational state. This empirical
function was used to normalize observed signals to the laser pulse energy. Note that the ionization efficiency is nearly identical when probing different vibrational states since the ionization cross section of the $\Lambda^2 \Sigma^+$ state is only weakly wavelength dependent between $\lambda_{\text{MPI}} = 225$ and 324 nm (Refs. 35, 36, and 41) and all vibrational states are excited to the $\Lambda^2 \Sigma^+$ ($v_\Sigma = 0$) state prior to the ionization step. Furthermore, one-color (1+1) REMPI was always used with laser pulse energies substantially above 1 mJ, ensuring saturation of the resonant transition in the $\gamma$-band. Thus, the (1+1) REMPI signal originating from different vibrational states is independent of the Franck-Condon factors $Q(v_\Sigma, v)$ of the corresponding vibronic transitions.

The gain of the MCP, $\Gamma_\gamma$, varies as the voltage across the MCP is adjusted to optimize conditions for the detection of each vibrational state. The gain of the MCP is set to a value that allows for a satisfactory signal to noise ratio while avoiding saturation of the MCP. The gain factor, $\Gamma_\gamma$, was experimentally measured over a wide range of voltages, $V$, and is given as follows:

$$\Gamma \propto V^{1.78 \pm 0.45}. \tag{10}$$

Equation (10) was valid for $1200 \text{ V} < V < 2000 \text{ V}$.

F. The density-to-flux conversion

As previously mentioned, knowledge of final velocity of the scattered molecules, $\langle \mu_f \rangle$, is used to convert the REMPI derived density measurement to flux, which is proportional to the state-to-state scattering probability. These velocities were derived from IR-UV double resonance TOF measurements in a fashion similar to previous work.32,33 The translational inelasticity, $\langle 1/2mu^2_{\text{channel}} \rangle$, for the vibrationally elastic scattering channel, NO ($v = 0 \rightarrow 0$), was found to be $\sim0.5$. For vibrationally inelastic channels, NO ($v = 0 \rightarrow 1,2$), an additional translational energy loss was seen, corresponding to $\sim8\%$ of the vibrational excitation energy gained by the molecule. A comprehensive report of T-V coupling during the course of vibrational excitation and relaxation of NO upon scattering from Au(111) is forthcoming.

Since the final translational energy is approximately independent of vibrational state, the density-to-flux conversion correction factor is negligible under nearly all of our conditions. An important exception is the lowest incidence translational energy of this work, $E_t = 0.11 \text{ eV}$. Here, the correction is significant since any T-V coupling represents a larger fraction of the translational energy.

IV. DISCUSSION

The derived vibrational excitation probabilities for NO($v = 0 \rightarrow 1$) and NO($v = 0 \rightarrow 2$) are shown in Fig. 10 and listed in Appendix B. The error bars on the experimental data were determined by estimating the statistical uncertainties in all input variables and then calculating their propagation into the absolute excitation probability, see Appendix C.

At all incidence energies, the vibrational excitation probabilities follow an Arrhenius dependence on surface temperature (solid lines) with an activation energy equal to the change of the vibrational energy. This is true for both the single and double quantum vibrational excitation. This Arrhenius surface temperature dependence is commonly attributed to the distribution of thermally excited EHPs which mediate vibrational excitation.7–9,12,13
In all cases the vibrational excitation is at least one order of magnitude higher for NO(v = 0→1) than for NO(v = 0→2). The population ratio between the two excited vibrational states is nearly independent of incidence energy. The fact that the vibrational excitation exhibits an Arrhenius surface temperature dependence at all incidence energies, with the activation energy equal to the vibrational spacing as well as that the relative excitation NO(v = 0→1) to that of NO(v = 0→2) is independent of incident energy indicates that over the wide translational energy and surface temperature range used in this study the predominant mechanism for vibrational excitation of NO scattering from Au(111) is electronically non-adiabatic coupling.

The solid lines of Fig. 10 demonstrate that the excitation probabilities follow an Arrhenius dependence on surface temperature and from this an Arrhenius pre-exponential factor can be obtained. The Arrhenius pre-factors are plotted vs. $E_i$ in Fig. 11. Error bars representing 90% confidence intervals were calculated according to the Student $t$-test. Due to background issues stemming from NO(v = 1) native in the incident beam (see above) excitation probabilities measured at $T_S = 300$ K have been neglected from the Arrhenius pre-factor comparison.

The Arrhenius pre-factors are useful as they indicate the intrinsic strength of the nonadiabatic coupling that induces vibrational excitation, decoupling it from the factors that only reflect the EHP thermal population distribution. They are limited to values between 0 and 1. An upper value of 1 indicates that the coupling is strong enough to allow full equilibration between vibration and the EHP bath on the time scale of the collision. The values obtained in this work, ranging from 0.17 to 0.85, represent strong coupling between the molecular vibration and the EHP bath of the metal, for example, in comparison to vibrational excitation of HCl(v = 0→1) when scattered from Au(111), where pre-factors of 0.002 were derived. Consistent with earlier observations, there is a strong incidence energy dependence in nonadiabatic vibrational excitation. At the highest incidence energies, the excitation probabilities approach those expected for thermal equilibrium with the surface.

At most incidence translational energies, the ratio between the Arrhenius pre-factors for NO(v = 0→2) and NO(v = 0→1) is near 0.8. The similar magnitude of the pre-exponential factors for NO(v = 0→1) and for NO(v = 0→2) vibrational excitation hints at the mechanism of direct overtone vibrational excitation. Should $v = 2$ be populated by a sequential mechanism–NO(v = 0→1→2)–the pre-exponential factor for $\Delta v = 2$ would be on the order of the square of that for $\Delta v = 1$, however, as seen in Fig. 11 the pre-exponential is roughly the same for both NO(v = 0→2) and NO(v = 0→1). The similarity in magnitude between single and overtone excitation pre-exponential factors indicates that NO(v = 0→2) excitation occurs primarily via direct overtone transitions.

One interesting implication of our results, which can be seen in Fig. 11, concerns the extrapolation to $E_i = 0$. The results seem to suggest that the intrinsic excitation probability does not vanish at zero incidence energy of translation. This might be evidence for a steering effect, since theory shows that when NO approaches Au(111) nitrogen atom first, electronically nonadiabatic coupling is enhanced. However, this implication should be considered carefully. At low incidence energies of translation, the density-to-flux correction described above is large. Any errors in its evaluation might alter the results at the lowest values of $E_i$ enough to change this qualitative conclusion. Improved experiments that might resolve this uncertainty are currently underway.

In addition, if trapping desorption were to play an important role, it might alter the interpretation of these observations especially at the lowest values of $E_i$ used in this work. The
trapping probability of NO scattering on Au(111) has been previously measured\textsuperscript{44} and IESH dynamical calculations\textsuperscript{19} using a potential surface derived from density functional theory (DFT) (Ref. 20) give reasonable agreement with these measurements. The well depth of this DFT derived potential surface is 0.13 eV. We can estimate the residence time of trapped NO on the Au(111) surface using statistical models\textsuperscript{44} and these show that, not surprisingly, the residence time in this case can be substantially longer (1–10 ps time scale) than the interaction time in direct scattering. Of course, the increased residence time might allow for more probable vibrational excitation.

The angular distributions (see Figs. 6 and 12) for both NO(v = 0 → 1) and NO(v = 0 → 2) scattering channels at E\textsubscript{i} = 0.11 eV are broader than those seen at higher incidence energies, an observation that might suggest trapping desorption is playing a role here. This alone does not indicate that trapping desorption is the predominant mechanism because as the incidence kinetic energy is lowered, the energy of a hot surface (1000 K corresponds to 0.09 eV) becomes comparable to the incident translational energy which could lead to a dramatic broadening of the scattered angular distribution. However, the fact that the angular distribution at E\textsubscript{i} = 0.11 eV, \(\cos^2(\theta)\), is virtually indistinguishable from the expectation of trapping desorption, \(\cos^{2.5}(\theta)\), is a strong indication that at the lowest incidence energy trapping desorption is the predominant mechanism.

V. CONCLUSIONS

We have provided a comprehensive description of the method for deriving absolute vibrational excitation probabilities from molecular beam surface scattering experiments. The experimental aspects concerning spectral, angular, and temporal distributions as well as influence of laser pulse energy on the derived absolute vibrational excitation probabilities were presented and discussed in detail. Arrhenius pre-factors, a measure of the strength of the vibration electron coupling, were extracted from the vibrational excitation probabilities and these showed a strong dependence on the incidence energy. The coupling between vibration of the molecule and EHPs of the metal is strong enough at higher incidence energies to allow approach to the thermal limit of vibrational excitation both for NO(v = 0 → 1) and NO(v = 0 → 2) channels. The similar magnitudes of the Arrhenius pre-factors for single and double quantum vibrational excitation suggests that NO(v = 0 → 2) excitation occurs predominantly via direct overtone excitation. In addition to quantitative evaluation of absolute vibrational excitation probabilities, the rotational distributions and angular distributions provide an important handle to study the scattering dynamics in the NO/Au(111) system. The described experimental approach generates an extensive set of data to which theoretical models of electronically nonadiabatic phenomena can be compared.

ACKNOWLEDGMENTS

C.B., D.J.A., and A.M.W. acknowledge support from the Alexander von Humboldt Foundation.

APPENDIX A: ANGULAR DISTRIBUTION WIDTH PARAMETERS

<table>
<thead>
<tr>
<th>Incidence energy (E\textsubscript{i}/eV)</th>
<th>Surface temperature (T\textsubscript{s}/K)</th>
<th>Angular width parameter ((\sigma/)°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(v = 0 → 0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11</td>
<td>303</td>
<td>20</td>
</tr>
<tr>
<td>0.28</td>
<td>303</td>
<td>18</td>
</tr>
<tr>
<td>0.41</td>
<td>912</td>
<td>16</td>
</tr>
<tr>
<td>0.41</td>
<td>310</td>
<td>17</td>
</tr>
<tr>
<td>0.41</td>
<td>303</td>
<td>18</td>
</tr>
<tr>
<td>0.63</td>
<td>303</td>
<td>17</td>
</tr>
<tr>
<td>0.93</td>
<td>946</td>
<td>16</td>
</tr>
<tr>
<td>0.93</td>
<td>652</td>
<td>15</td>
</tr>
<tr>
<td>0.93</td>
<td>308</td>
<td>17</td>
</tr>
<tr>
<td>0.93</td>
<td>303</td>
<td>18</td>
</tr>
<tr>
<td>0.93</td>
<td>303</td>
<td>19</td>
</tr>
<tr>
<td>1.05</td>
<td>303</td>
<td>18</td>
</tr>
</tbody>
</table>

| NO(v = 0 → 1)                        |                                       |                                 |
| 0.11                                 | 973                                  | 22                              |
| 0.11                                 | 633                                  | 23                              |
| 0.11                                 | 323                                  | 19                              |
| 0.28                                 | 973                                  | 22                              |
| 0.28                                 | 633                                  | 20                              |
| 0.28                                 | 323                                  | 19                              |
| 0.41                                 | 943                                  | 18                              |
| 0.41                                 | 543                                  | 18                              |
| 0.63                                 | 973                                  | 20                              |
### APPENDIX B: ABSOLUTE VIBRATIONAL EXCITATION PROBABILITIES

<table>
<thead>
<tr>
<th>Incidence energy (Ei/eV)</th>
<th>Surface temperature (Ts/K)</th>
<th>Excitation probability</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(v = 0 → 1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11</td>
<td>973</td>
<td>1.1 × 10^{-2}</td>
<td>5.5 × 10^{-3}</td>
</tr>
<tr>
<td>0.11</td>
<td>873</td>
<td>8.0 × 10^{-3}</td>
<td>4.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.11</td>
<td>753</td>
<td>4.0 × 10^{-3}</td>
<td>2.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.11</td>
<td>633</td>
<td>2.0 × 10^{-3}</td>
<td>1.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.11</td>
<td>503</td>
<td>7.0 × 10^{-4}</td>
<td>3.5 × 10^{-4}</td>
</tr>
<tr>
<td>0.12</td>
<td>973</td>
<td>1.2 × 10^{-2}</td>
<td>6.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.11</td>
<td>873</td>
<td>8.0 × 10^{-3}</td>
<td>4.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.11</td>
<td>753</td>
<td>7.0 × 10^{-3}</td>
<td>3.5 × 10^{-3}</td>
</tr>
<tr>
<td>0.11</td>
<td>633</td>
<td>3.0 × 10^{-3}</td>
<td>1.5 × 10^{-3}</td>
</tr>
<tr>
<td>0.28</td>
<td>493</td>
<td>1.2 × 10^{-3}</td>
<td>6.0 × 10^{-4}</td>
</tr>
<tr>
<td>0.28</td>
<td>323</td>
<td>2.0 × 10^{-4}</td>
<td>1.0 × 10^{-4}</td>
</tr>
<tr>
<td>0.41</td>
<td>1073</td>
<td>3.0 × 10^{-2}</td>
<td>1.5 × 10^{-2}</td>
</tr>
<tr>
<td>0.41</td>
<td>973</td>
<td>2.0 × 10^{-2}</td>
<td>1.0 × 10^{-2}</td>
</tr>
<tr>
<td>0.41</td>
<td>878</td>
<td>1.6 × 10^{-2}</td>
<td>8.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.41</td>
<td>776</td>
<td>1.1 × 10^{-2}</td>
<td>5.5 × 10^{-3}</td>
</tr>
<tr>
<td>0.41</td>
<td>673</td>
<td>6.0 × 10^{-3}</td>
<td>3.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.41</td>
<td>673</td>
<td>7.0 × 10^{-3}</td>
<td>3.5 × 10^{-3}</td>
</tr>
<tr>
<td>0.41</td>
<td>573</td>
<td>2.0 × 10^{-3}</td>
<td>1.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.41</td>
<td>573</td>
<td>2.0 × 10^{-3}</td>
<td>1.0 × 10^{-3}</td>
</tr>
<tr>
<td>0.41</td>
<td>473</td>
<td>2.0 × 10^{-3}</td>
<td>1.0 × 10^{-3}</td>
</tr>
</tbody>
</table>

These parameters refer to Eq. (8).
APPENDIX C: PROPAGATION OF ERRORS

The input variables and their estimated relative uncertainties are the integrated signal intensities, $\text{SIG}_i(j,j_1,\beta_1,\gamma,\tau_v)$ (1%), the mean velocities, $(u_v)$ (5%), the angular dilution corrections, $\Theta_i(\theta_0)$ (5%), the temporal dilution corrections, $\Delta_i(\tau_v)$ (5%), the MCP voltages, $U_v$ (0.5%), and the mean laser pulse energies, $I_v$ (20%). Note that in Eq. (7), which represents the derived excitation probabilities in terms of these quantities, all of these variables appear for $v = 0$ and for $v = 1, 2, 3, $ that is in the numerator and in the denominator.

The propagation of experimental uncertainties $\Delta x_i$ into the excitation probability $P$ was calculated according to

$$
\Delta P = \sqrt{\sum (\frac{\partial P}{\partial x_i} \Delta x_i)^2}.
$$

As $P$ is of the form $P = \prod x_i^{n_i}$, the relative uncertainty may be expressed as a function of the relative uncertainties of the input variables as $\Delta P / P = \sqrt{\sum (n_i \Delta x_i / x_i)^2}$, where the exponents $n_i$ are $\pm 1$ except for $U_v$ $(n = 17.8)$ and $I_v$ $(n = 1.66)$.

For the given estimated uncertainties on the input parameters, we find that $\Delta P / P \sim 50\%$. These uncertainties are listed in Appendix B. The largest contributions originate from fluctuations in the laser pulse energy.

23. In principle, a more precise treatment for the density-to-flux conversion would utilize the full velocity distribution. In practice under the experimental conditions used here this is not necessary as the density-to-flux conversion is rather small. Experimentalists treating other systems with this or other experimental methods should pay strict attention to the approximation used in this work and whether it still holds in other cases.
26. Preliminary results show that NO(v = 3) is at least a factor of 10 less populated than NO(v = 2) under the experimental conditions used in this work.