Calculations of scattering of N_2 molecules from Ru(0001)

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As a part of an extensive study by the Odense group of N_2 interactions with the Ru(0001) surface Mortensen *et al.* have reported detailed measurements for state resolved inelastic scattering.[1] This system is of current interest in debates concerning the applicability of the Born-Oppenheimer approximation in the interaction of molecules with metal surfaces. Calculations of N_2 dissociation based on density functional theory predict very efficient energy loss to electronic excitations in Ru(0001),[2] while classical trajectory calculations indicate that multidimensional effects associated with translational and rotational motions are much more important than nonadiabatic effects.[3]

Here, these scattering data are compared to calculations using a theoretical model that has been useful in explaining surface collisions in other systems involving small molecular projectiles. This theory, which is presented in detail elsewhere,[4–6] is a mixed classical-quantum treatment of surface scattering in which the translational and rotational degrees of freedom are treated with classical mechanics while the excitation of internal molecular vibrational modes is treated quantum mechanically. The interaction potential is chosen to be a strongly repulsive barrier whose corrugation vibrates under the influence of the underlying target atoms.

The most important and accurate measurements made were for the average final translational energy normal to the surface $\langle E_{fn}^T \rangle$ as a function of final rotational energy E_f^R. These are shown in Fig. 1(a) for two different energies and incident beam angles, $E_i^T = 1.5$ eV with $\theta_i = 19°$ and $E_i^T = 2.4$ eV with $\theta_i = 0°$ and the surface temperature is 610 K for all data shown here. These are compared with two sets of calculations, one using the mass Ru as the surface mass and the other with an effective surface mass 2.3 times that of a single Ru atom. For all calculations the value of the velocity parameter is 1000 m/s. Only qualitative agreement with the negative correlation between $\langle E_{fn}^T \rangle$ and E_f^R is obtained using the smaller mass. However, with the larger effective surface mass quantitative agreement is obtained, and this holds true for essentially all of the comparisons presented here.

Figure 1(b) shows a different way of presenting the negative correlation of Fig. 1(a) that includes the effects of energy transfer to the other degrees of freedom of the scattered molecules. Plotted in Fig. 1(b) as a function of E_f^R is the quantity $\langle \Delta E_s \rangle = E_{in} - \langle E_{fn}^T \rangle - \langle \Delta E_{\parallel}^T \rangle - \langle \Delta E^R \rangle - \langle \Delta E_v \rangle$. The quantities $\langle \Delta E_{\parallel}^T \rangle$, $\langle \Delta E^R \rangle$, and $\langle \Delta E_v \rangle$ are the average transfer of energy to parallel translational, rotational, and vibrational degrees of freedom, respectively. Again, the calculations with the larger effective surface mass give reasonable quantitative agreement with experiment. In the calculations $\langle \Delta E_v \rangle$ was negligible, in agreement with experimental observations. It should be noted that Ref. 1 also reported two data points taken at $E_i^T = 2.7$ eV and $\theta_i = 19°$ with which our calculations also agree but for clarity are not shown.

The incident energy dependence of the average final translational energy is shown in Fig. 2 where the normalized energy difference $1 - \langle E_{fn}^T \rangle / E_{in}^T$ is plotted for several incident beam angles as marked. The data for $\theta_i = 40°$ denoted by asterisks and those for $\theta_i = 50°$ denoted by cross symbols were extracted from Ref. 7 by the authors of Ref. 1. Calculations are shown for the two masses and reasonable agreement is obtained with the $\theta_i = 50°$ data for the higher mass. The data at angles other than 50° are only qualitatively explained, but better agreement is with the larger effective surface mass.

The average energy transfer perpendicular to the plane of scattering $\langle \Delta E_x^T \rangle$ is shown in Fig. 3 as a function of incident energy E_i with an incident angle $\theta_i = 19°$. The calculations for the larger surface mass show the biggest out-of-plane energy transfers for incident energies greater than 0.4 meV, as expected since a larger surface mass leads to less overall energy transfer and hence higher translational energy in all directions of scattered particles. In this case the better overall agreement with experiment is for an effective mass equal to that of one Ru atom.

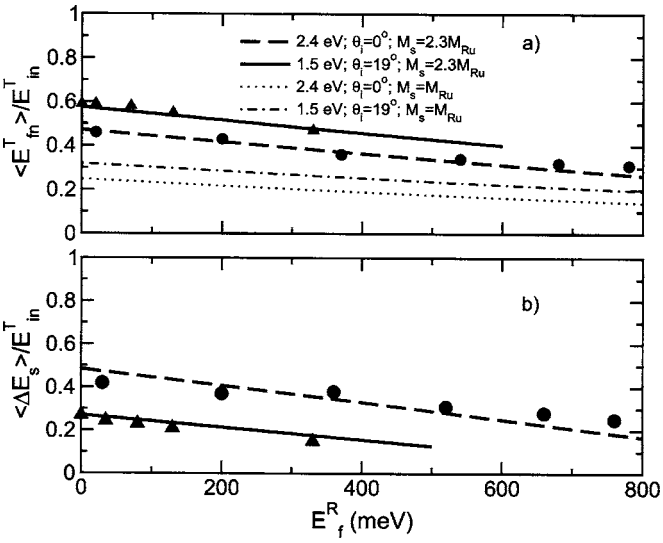

FIG. 1. (a) The average normal translational energy $\langle E_{fn}^T \rangle / E_{in}^T$ as a function of final rotational energy E_f^R. (b) Average fractional energy loss to the surface $\langle \Delta E_s \rangle / E_{in}^T$ vs E_f^R. Incident beam conditions are $E_i = 2.4$ eV and $\theta_i = 0°$ with data shown as circles and $E_i = 1.5$ eV and $\theta_i = 19°$ shown as triangles.

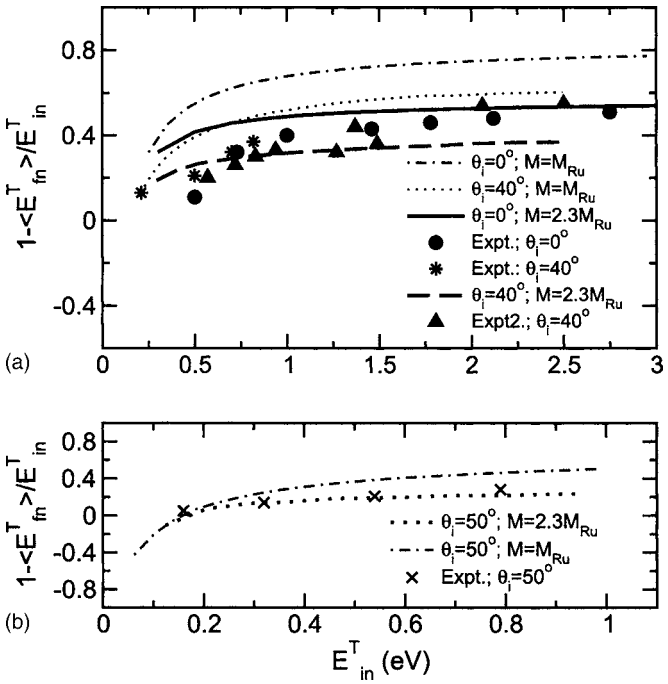

FIG. 2. The normal translational energy loss as a function of the normal incident energy E_{in}. The top panel is for $\theta_i=40°$ and $\theta_i=0°$ and bottom panel is for $\theta_i=50°$.

Rotational temperatures of the scattered spectra as functions of incident energy are compared with the calculated predictions in Fig. 4 and again better quantitative agreement is obtained with a larger effective mass.

Reasonable agreement of the present theory with observations is obtained, but with the exception of parallel energy transfer out of the scattering plane, only when a larger effective mass is used for the Ru surface. The collective effect, implied by a larger effective mass, has been noted in several other attempts using simpler models to compare calculations with a variety of atomic[8,9] and molecular[10] scattering measurements from Ru surfaces. For molecular scattering from other metal surfaces a larger effective mass has not been necessary using present theoretical methods.[1–6,11] The fact that a larger effective mass is not needed for the case of energy transfer in directions parallel to the surface is suggestive that the collective effect involves Ru atoms in layers below the surface, and not parallel to the surface.

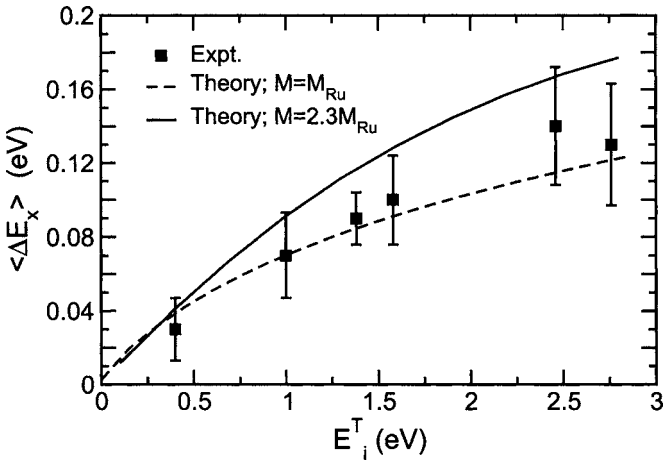

FIG. 3. The average energy change $\langle \Delta E_x^T \rangle$ associated with the transfer of momentum perpendicular to the plane of scattering.

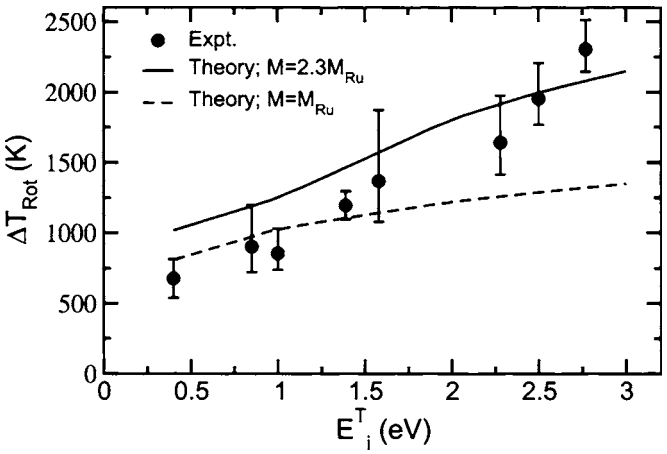

FIG. 4. The difference between the final and initial rotational temperatures $\Delta T_{\rm rot}$ as a function of the incident translational energy E_i.

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[1] H. Mortensen, E. Jensen, L. Diekhöner, A. Baurichter, A. C. Luntz, and V. V. Perunin, J. Chem. Phys. **118**, 11200 (2003); a review of other N_2 surface interaction papers is given here.
[2] A. C. Luntz and M. Persson, J. Chem. Phys. **123**, 074704 (2005).
[3] C. Dáz, J. K. Vincent, G. P. Krishnamohan, R. A. Olsen, G. J. Kroes, K. Honkala, and J. K. Nørskov, Phys. Rev. Lett. **96**, 096102 (2006).
[4] I. Iftimia and J. R. Manson, Phys. Rev. Lett. **87**, 093201 (2001); I. Iftimia and J. R. Manson, Phys. Rev. B **65**, 125412 (2002).
[5] H. Ambaye, J. R. Manson, O. Weiße, C. Wesenberg, M. Binetti, and E. Hasselbrink, J. Chem. Phys. **121**, 1901 (2004).
[6] H. Ambaye and J. R. Manson, J. Chem. Phys. **125**, 084717 (2006).
[7] D. C. Papageorgopoulos, B. Berenbak, M. Verwoest, B. Riedmüller, S. Stolte, and A. W. Kleyn, Chem. Phys. Lett. **305**, 401 (1999).
[8] B. Berenbak, S. Zboray, B. Riedmüller, D. C. Papageorgopoulos, S. Stolte, and A. W. Kleyn, Phys. Chem. Chem. Phys. **4**, 68 (2002).
[9] W. W. Hayes and J. R. Manson, Phys. Rev. B (unpublished).
[10] B. Riedüller, I. M. Ciobîcă, D. C. Papageorgopoulos, B. Berenbak, R. A. Van Santen, and A. W. Kleyn, Surf. Sci. **465**, 347 (2000).
[11] I. Moroz and J. R. Manson, Phys. Rev. B **71**, 113405 (2005).