Effect of the Ar–Ni(s) potential on the cross section for Ar + CH 4 / Ni \{111\} collision-induced desorption and the need for a more accurate CH 4 / Ni \{111\} potential

Lipeng Sun, *Northwestern University*
Kirk A. Peterson, *Washington State University*
Yuri Alexeev, *Pacific Northwest National Laboratory*
Theresa L. Windus, *Pacific Northwest National Laboratory*
James Kindt, *Emory University*, et al.

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Effect of the Ar–Ni(s) potential on the cross section for Ar+CH$_4$/Ni{$^{111}$} collision-induced desorption and the need for a more accurate CH$_4$/Ni{$^{111}$} potential

Lipeng Sun  
Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Kirk A. Peterson  
Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

Yuri Alexeev and Theresa Windus  
Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352

James Kindt  
Department of Chemistry, Emory University, Atlanta, Georgia 30322

William L. Hase  
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-4106

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In a previous paper [L. Sun, P. de Sainte Claire, O. Meroueh, and W. L. Hase, J. Chem. Phys. 114, 535 (2001)], a classical trajectory simulation was reported of CH$_4$ desorption from Ni{$^{111}$} by Ar-atom collisions. At an incident angle $\theta_i$ of 60° (with respect to the surface normal), the calculated collision-induced desorption (CID) cross sections are in excellent agreement with experiment. However, for smaller incident angles the calculated cross sections are larger than the experimental values and for normal collisions, $\theta_i = 0^\circ$, the calculated cross sections are approximately a factor of 2 larger. This trajectory study used an analytic function for the Ar + Ni(s) intermolecular potential which gives an Ar–Ni{111} potential energy minimum which is an order of magnitude too deep. In the work reported here, the previous trajectory study is repeated with an Ar + Ni(s) analytic intermolecular potential which gives an accurate Ar–Ni{111} potential energy minimum and also has a different surface corrugation than the previous potential. Though there are significant differences between the two Ar + Ni(s) analytic potentials, they have no important effects on the CID dynamics and the cross sections reported here are nearly identical to the previous values. Zero-point energy motions of the surface and the CH$_4$–Ni(s) intermolecular modes are considered in the simulation and they are found to have a negligible effect on the CID cross sections. Calculations of the intermolecular potential between CH$_4$ and a Ni atom, at various levels of theory, suggest that there are substantial approximations in the ab initio calculation used to develop the CH$_4$+Ni{111} potential. The implication is that the differences between the trajectory and experimental CID cross sections may arise from an inaccurate CH$_4$+Ni{111} potential used in the trajectory simulation. © 2005 American Institute of Physics. [DOI: 10.1063/1.1829993]

I. INTRODUCTION

In a previous paper$^1$ a classical trajectory simulation of the collision-induced desorption (CID) of methane from Ni{111} was reported. The classical trajectories were integrated with analytic potential energy functions that were either determined by fitting ab initio data or taken from previous work.$^{2,3,5}$ The potential energy function for the system is written as

$$V = V_{Ni} + V_{ArNi} + V_{CH_4} + V_{CH_4Ni} + V_{ArCH_4}$$

(1)

Analytic functions developed previously were used for the nickel surface Ni(s)$^2$ and the Ar–Ni(s) interaction,$^3$ i.e., $V_{Ni}$ and $V_{ArNi}$, respectively. An analytic function, developed by Duchovic and co-workers,$^4$ was used for the CH$_4$ intramolecular potential $V_{CH_4}$. The potential for the CH$_4$–Ni(s) physisorption interaction $V_{CH_4Ni}$ was derived by fitting ab initio calculations by Yang and Whitten$^5$ for CH$_4$ interacting with an 88 atom Ni cluster. An analytic Ar+CH$_4$ intermolecular potential was developed by fitting MP2/aug-cc-pVTZ calculations for this system. As shown in Fig. 1, overall the trajectory CID cross sections versus collision energy $E_i$ are in good agreement with experiment.$^8$ However, for an incident angle $\theta_i = 0^\circ$ (with respect to the surface normal) the simulation cross sections are approximately a factor of 2 larger than the experimental values. Varying the CH$_4$–Ni(s) and Ar–CH$_4$ potentials, by modifying the fits to the ab initio calculations, had no significant effects on the calculated cross sections.

A possible shortcoming of the above trajectory study is that the Ar–Ni(s) analytic function gives an Ar–Ni{111} potential energy minimum that is about an order of magnitude...
too deep as compared to experiment. It is possible that this artificially high attractive interaction between Ar and Ni(s) adds additional translational energy to the incoming Ar atom, particularly in the surface normal direction, which increases the cross section at low incident angle. Because of this possible effect, it is important to reinvestigate the Ar + CH₄/Ni{111} CID dynamics with a more accurate potential. In this article, we report results obtained from the Ar–Ni(s) potential developed by Kindt and Tully,¹ which gives an accurate representation of the Ar/Ni{111} potential energy minimum.

II. POTENTIAL ENERGY FUNCTION

The Kindt/Tully Ar–Ni(s) potential is represented by a pairwise Morse function of the form

\[
V = D \left[ 1 - \exp \left( - \beta (r - r_0) \right) \right]^2
\]

and is obtained by fitting the Morse parameters to the experimental Ar/Ni surface binding energy¹⁰ and to scattering data.¹¹,¹² The parameters are \( D = 5.286 \times 10^{-3} \text{ eV} \), \( \beta = 1.9 \text{ Å}^{-1} \), and \( r_0 = 3.9 \text{ Å} \). For the 439 atom and four-layer model of the Ni{111} surface used in this simulation, the Ar atom sits in a hollow site, with a binding energy of \(-0.6 \text{ kcal/mol}\) and a height 3.6 Å above the outer layer of the surface. For the Ar–Ni(s) potential used in the previous trajectory study, these two properties of the potential energy minimum are \(-11.4 \text{ kcal/mol}\) and 2.7 Å. Also, as shown in Fig. 1, there is a substantial difference in the surface corrugation¹³ of the two potentials. The corrugation of the previous potential is 0.27 Å, while it is 0.14 Å for the current potential. Analyses of energy transfer in gas-surface collisions with washboard models¹³,¹⁴ show that energy transfer to the surface becomes more efficient as the surface corrugation is increased.

FIG. 1. Potential energy contour plots for Ar interacting with the Ni{111} surface. Contour labels are in kcal/mol. Note the different x and y scales. (a) Ar+Ni{111} potential used in the previous study, Ref. 1; (b) Ar+Ni{111} potential used in this work.

III. CLASSICAL TRAJECTORY PROCEDURE

The classical trajectory simulations were carried out in the same manner and with the same initial conditions as the previous work.¹ The most accurate I-models were used for the Ar/CH₄ and CH₄/Ni(s) potentials. However, as shown previously,¹ the less accurate III-models give CID cross sections which are statistically the same. To describe the 46 K experimental temperature,⁸ vibrational energy was not added to the Ni{111} cluster model, CH₄, or the CH₄–Ni(s) intermolecular modes. The system was initially placed in its classical potential energy minimum without zpe because the unphysical flow of zpe from CH₄ or the surface or between the intermolecular modes could result in artificial CH₄ desorption.¹⁵,¹⁶ The effect of releasing these constraints is discussed below.

IV. TRAJECTORY RESULTS

The \( b_{\text{max}} \) values calculated for CID (see Ref. 1 for definition), with this new Ar–Ni(s) potential, range from 1.4 Å for \( \theta_i = 0° \) and \( E_i = 12 \text{ kcal/mol} \) to 6.0 Å for \( \theta_i = 60° \) and \( E_i = 40 \text{ kcal/mol} \). Cross sections are calculated at \( \theta_i = 0° \) with \( E_i = 12, 16, 24, \) and 32 kcal/mol, \( \theta_i = 30° \) with \( E_i = 18 \) and 32 kcal/mol, and \( \theta_i = 60° \) with \( E_i = 16 \) and 40 kcal/mol. The cross sections, with their standard deviations, are plotted in Fig. 2 versus the normal initial energy \( E_i^n = E_i \cos^2 \theta \). Also included in Fig. 2 are the experimental data and the results from the previous trajectory calculation.¹

As shown in Fig. 2, there is overall excellent agreement between the previous and current CID cross sections. Using the new Ar–Ni(s) potential does not remove the nearly fac-
tor of 2 difference between the calculated and experimental cross sections at $\theta_i = 0^\circ$. However, for the lowest $E_i$ of 12 kcal/mol investigated at $\theta_i = 0^\circ$ and where experimental results are not available, the current cross section is 3.5 times smaller than the previous value. Thus, the new more accurate Ar–Ni$(s)$ potential substantially lowers the calculated CID cross section at low $E_i$ for collisions with an incident angle of $0^\circ$, but has only a small effect on the calculated cross section at other $E_i$ and $\theta_i$. Though the new Ar–Ni$(s)$ potential has a much shallower potential energy minimum of $-0.6$ kcal/mol compared to the 11.4 kcal/mol minimum of the previous potential and also has a substantially different corrugation, these different properties do not have an appreciable effect on the higher energy CID cross sections. This result is understandable from the results of the previous trajectory study, which show that for $\theta_i = 0^\circ$ CID occurs by collisions in which the Ar atom first strikes CH$_4$. For these events the nature of the Ar–Ni$(s)$ potential seems to be unimportant. For large collision angles, e.g., $60^\circ$, and collision energies larger than 35 kcal/mol, there is a small fraction of CID trajectories for which the Ar atom rebounds off Ni$(s)$ and then strikes CH$_4$. The Ar–Ni$(s)$ well depth and corrugation may affect their dynamics. However, they are insignificant for the $\theta_i$ and $E_i$ considered in this work.

V. THERMAL AND ZERO-POINT ENERGY EFFECTS

The above simulations were performed with a four-layer slab of 439 Ni atoms representing the Ni[111] surface. The surface was not thermostated and any energy transferred to the surface remained in this slab. To determine whether dissipating energy from the slab would affect the CID cross sections, the simulations at $\theta_i = 0^\circ$ and $E_i$ of 16 and 24 kcal/mol were repeated with a Berendsen heat bath$^{17}$ attached to the bottom layer of the slab. As discussed above, to model the 46 K low temperature experiment$^6$ the Ni atoms in the slab were placed at their classical minimum and the heat bath target temperature of the bottom layer remained at 0 K. A maximum rate for energy dissipation was introduced by resetting the velocities of the bottom layer atoms to 0 at each integration step. Simulations were performed by scaling only the $z$ components of the atoms’ velocities and also by scaling all three components of the velocities.

This scaling had a negligible effect on the CID cross sections. At $E_i = 16$ kcal/mol and with velocity scaling in only the $z$ direction, the cross section changes by only 3%, with scaling in all three directions the difference is 1%. A similar result is found at $E_i = 24$ kcal/mol. With scaling in only the $z$ direction, the cross sections differ by only 1% and there is no difference if the scaling is in all three directions. For both the $E_i$ of 16 and 24 kcal/mol simulations, the kinetic energy of the atoms in the bottom layer remain small throughout the duration of the trajectories, so there is little energy to dissipate from these boundary atoms. The conclusion reached from these simulations with velocity scaling, is that dissipation of energy from the 439 atom model of the surface does not have an important effect on the CID cross sections.

Each of the above simulations was performed with the CH$_4$/Ni$(s)$ system placed in its classical potential energy minimum without the addition of zpe or the 46 K temperature of the experiments.$^5$ There are two possible effects of zpe on the CID dynamics. One is the unphysical flow of zpe$^{15,16}$ which could possibly artificially enhance CH$_4$ desorption. This is why zpe was excluded from the simulations. On the other hand, studies of the effects of zpe on intramolecular vibrational energy redistribution$^{18}$ and unimolecular dissociation pathways$^{19}$ show that zpe may make the chemical dynamics more chaotic, opening more channels for energy relaxation. The previous study$^1$ shows that adding zpe to the CH$_4$–Ni$(s)$ intermolecular modes does not affect the CID cross sections. To see if adding energy to Ni$(s)$ in the trajectory initial conditions enhances energy transfer to Ni$(s)$, as Ar collides with CH$_4$, and thus reduces the CID cross section, two additional sets of simulations were performed; i.e., one with zpe and the other with a classical energy of RT ($T = 46$ K) added to each of the surface modes. For these simulations CID cross sections were calculated at $\theta_i = 0^\circ$ with $E_i$ of 16 and 24 kcal/mol. They were found to be the same (within statistical uncertainties) of those calculated above without zpe or RT added to the surface modes. Thus, not adding energy to Ni$(s)$ in the trajectory initial conditions cannot explain the differences between the experimental and simulation CID cross sections.

VI. THE CH$_4$/Ni$(s)$ INTERMOLECULAR POTENTIAL

In contrast to the disagreement found here between classical trajectory and experimental cross sections for Ar + CH$_4$/Ni[111] collision-induced desorption, there is excellent agreement between experiment and trajectory simulations for collisions of the Cr$^+$ (CO)$_6$ ion$^{20}$ and the Ne rare gas atom$^{21}$ with hydrocarbon surfaces. For these two systems the trajectory and experimental energy transfer distributions are very similar, and it is difficult to explain why classical trajectory simulations agree with experiment for these two systems, but not for the system studied here. A possible source of error is an inaccurate intermolecular potential between CH$_4$ and the Ni surface. The CH$_4$, Ni$(s)$, and Ar/CH$_4$ (Ref. 1) potentials used in the simulation are excellent representations of ab initio calculations and/or experiments and they should not affect the accuracy of the classical trajectory simulation. However, the CH$_4$–Ni$(s)$ intermolecular potential must accurately describe energy transfer to the Ni surface as Ar atom collides with CH$_4$. If an inaccurate representation of this potential restricts energy transfer to the Ni surface, the amount of energy remaining in the CH$_4$–Ni$(s)$ intermolecular interaction may be too large and could artificially increase the CID cross section.

The analytic function used for the CH$_4$/Ni$(s)$ intermolecular potential was derived from ab initio calculations for CH$_4$ interacting with an 88 atom Ni cluster.$^5$ An embedded model was used for the Ni cluster in which different basis sets were used for different groups of Ni atoms. A [1s–2p] core potential and valence 3$s$, 3$p$ double-$\zeta$ 3$d$, 4$s$, and 4$p$ orbitals were included for the Ni atom most strongly interacting with CH$_4$. A double-$\zeta$ $s$ and $p$ basis, augmented with a set of $d$ polarization functions, was used for the carbon atom. A double-$\zeta$ basis was used for the hydrogens. These
basis were used in configuration interaction (CI) calculations, with single and double excitations (i.e., CISD), for the CH$_4$/Ni-cluster system. These \textit{ab initio} calculations give a potential energy minimum of $-0.7$ kcal/mol for CH$_4$ physisorbed on Ni[111]. In contrast, Szulciewski and Levis$^{22}$ modeled the Ar+CH$_4$/Ni[111] experiments of Ceyer and co-workers$^8$ and determined a value of $-2.7$ kcal/mol for the physisorption binding energy. To construct the analytic CH$_4$/Ni[111] potential used for the trajectory calculation,$^4$ the \textit{ab initio} CH$_4$/Ni[111] potential was shifted by 2.0 kcal/mol to give a potential energy minimum of $-2.7$ kcal/mol.

An approach for checking the accuracy of the above CH$_4$/Ni-cluster calculation and ensuring the determination of an accurate potential for CH$_4$ interacting with a Ni surface would be to increase the size of the cluster model and the level of \textit{ab initio} theory until the calculated results are converged. This would be a formidable calculation and was not pursued here. Instead, the intermolecular potential between CH$_4$ and a single Ni atom was calculated using four different levels of \textit{ab initio} theory and the resulting potential curves were compared. One level of theory is CISD with a cc-pVDZ basis$^7$ on all atoms and a [1s-2p] effective core potential (ECP) for the Ni atom.$^{23}$ This is a close representation of the level of theory used by Yang and Whitten for their CH$_4$/Ni-cluster calculation.$^5$ They used CISD theory with a modified Wachters basis set$^{24}$ for which valence 4s, 4p, and 3d functions were explicitly included.$^{25}$ In the cc-pVDZ basis set, 4f functions are included in addition to the valence 4s, 4p, and 3d functions. The other three \textit{ab initio} theories considered are CISD+Q (CISD with the Davidson correction$^{26}$), MRCI+Q (internally contracted multireference CISD with the Davidson correction$^{27}$), and R/UCCSD(T) (spin unrestricted singles and doubles coupled cluster theory with perturbative triples based on ROHF orbitals$^{28}$). The six configurations used for the MRCI+Q calculations are the parent HF configuration and five additional configurations to represent Ni $d^8 s^2$. Calculations were performed with a cc-pVTZ basis set,$^7$ as well as the cc-pVDZ basis, to determine the effect of the basis set on the results. All calculations were performed using the MOLPRO (Ref. 29) and NWChem (Ref. 30) quantum chemistry programs.

In calculating the Ni+CH$_4$ intermolecular potential curve, CH$_4$ was held fixed in its equilibrium geometry and the Ni–C distance varied along the system’s C$_3v$ symmetry axis, with Ni approaching the face of CH$_4$. The Ni atom’s ground state is a triplet and for all the calculations it was found that the triplet is 40–50 kcal/mol lower in energy than the singlet, depending on the distance between the Ni and C atoms. Therefore, all the potential energy curves presented here are for the triplet state of the Ni atom.

The calculated potential energy curves are given in Table I. There are both similarities and differences amongst the curves. The CISD+Q, MRCI+Q, and CCSD(T) long-range curves for the cc-pVDZ basis set are similar and for the “rough scan” have a minimum energy of $-0.20–-0.26$ kcal/mol at 4.5 Å. The CISD curve, which represents the level of theory used by Yang and Whitten,$^5$ is decidedly less attractive. There are interesting differences in the short-range potential curves. The MRCI+Q curves are most repulsive, while the CCSD(T) curve is least repulsive. Multi-reference effects become important at short Ni–C separations, which may in part explain the less repulsive CCSD(T) curve. The CISD and CISD+Q curves are intermediate. Interestingly, the CISD+Q curve is more attractive, but less repulsive, than the CISD curve. The effect of increasing the basis set size from cc-pVDZ to cc-pVTZ is to make the potential more attractive and less repulsive. However, the relative importance of these two effects depends on the level of theory.

<table>
<thead>
<tr>
<th>R (Å)</th>
<th>CISD</th>
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<th>MRCI+Q</th>
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$^4$The lowest three states of A' symmetry are given.

The electronic energy for separated Ni+CH$_4$ is listed in Table II for the different levels of theory. CCSD(T) gives the lowest energy and apparently best represents electron correlation for the long-range interaction. The CISD calculation, which models the Yang and Whitten study,$^5$ has an energy much higher than the others. These results, and an understanding of different theoretical methods, suggest that CCSD(T) is most accurate in the long-range, attractive region of the potential energy surface. Thus, the position and depth of the Ni–CH$_4$ potential minimum for the CCSD(T) theory was determined by performing additional calculations.
The CISD calculation, which models the method used by Yang and Whitten\(^2\) to determine the CH\(_4\)–Ni(s) potential, has a long-range potential different from those of the other theories and a short-range potential similar, but not equivalent, to those for the CISD+Q and MRCI+Q curves. All these short-range potentials have different curvatures as a function of the Ni–CH\(_4\) separation, which will affect CH\(_4\) + Ni(s) energy transfer. The uncertainty in the CH\(_4\)–Ni(s) intermolecular potential, used for the current simulations, may help to explain the difference between the classical trajectory and experimental cross sections for Ar + CH\(_4\)/Ni(s) CID at small \(\theta_i\). Energy transfer from Ar to CH\(_4\) and then to the Ni surface is expected to be most important for perpendicular collisions with the surface and it is for this incident angle that there is the greatest disagreement between the trajectory and experimental cross sections. It is expected that an accurate CH\(_4\)–Ni(s) intermolecular potential is required to accurately describe this energy transfer and in future work it will be important to consider a range of \textit{ab initio} approaches for developing this potential.

### VII. SUMMARY

In previous work\(^1\) a classical trajectory simulation was used to calculate the Ar + CH\(_4\)/Ni[111] CID cross section as a function of the incident collision energy \(E_i\) and angle \(\theta_i\). At large \(\theta_i\) there is excellent agreement between the simulation and previously reported\(^6\) experimental CID cross sections. However, for smaller \(\theta_i\) the simulation cross sections are larger than the experimental values. In the work presented here two analyses are performed to try to understand the origin of this difference. The Ar–Ni(s) analytic potential energy function used in the previous simulation gives an Ar–Ni[111] potential minimum which is an order of magnitude too deep. The simulations are repeated here with a more accurate Ar–Ni(s) potential,\(^7\) one which gives the correct potential minimum, and it is found that using this potential does not significantly alter the calculated higher energy CID cross sections. Trajectories may be adversely affected by the unphysical flow of zpe (Refs. 13 and 14) and different procedures were considered in the simulations for treating the zpe of CH\(_4\) and the Ni[111] surface model. However, at most, only insignificant changes were found in the calculated CID cross sections. Thus, neither using a more accurate Ar–Ni(s) potential energy function nor modifying the way CH\(_4\) and Ni[111] zpe is treated in the simulations significantly alters the calculated CID cross sections at small \(\theta_i\) and brings them into better agreement with experiment.

The origin of the difference between the experimental and simulated cross sections was further studied by considering the CH\(_4\)–Ni[111] intermolecular potential used in the simulations. This potential was calculated at the CISD level of theory using a relatively small basis set.\(^5\) The accuracy of this level of theory for the CH\(_4\)–Ni[111] system was investigated by comparing CISD, CISD+Q, MRCI+Q, and CCSD(T) calculations of the potential energy curve for the ground triplet state of Ni interacting with CH\(_4\). The results of these calculations suggest the CH\(_4\)–Ni[111] intermolecular potential used in the simulation is inaccurate. The basis set is too small and a level of theory higher than CISD is

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**TABLE II.** Electronic energy at different levels of theory for separated Ni + CH\(_4\). The calculations are for the ground state triplet potential energy surface. See Table I for an explanation of the MRCI+Q energies. The energies are in atomic units.

<table>
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<th>Theory</th>
<th>cc-pVDZ-PP</th>
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<tr>
<td>CISD</td>
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<td>210.611 559</td>
</tr>
<tr>
<td>CISD+Q</td>
<td>210.563 911</td>
<td>210.666 368</td>
</tr>
<tr>
<td>MRCI+Q</td>
<td>210.562 858</td>
<td>210.665 021</td>
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<tr>
<td>CCSD(T)</td>
<td>210.577 507</td>
<td>210.664 975</td>
</tr>
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</table>

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**TABLE III.** Ni–CH\(_4\) potential energy minimum. The calculations are performed at the CCSDs(T) level of theory and are for the ground state triplet potential energy surface.

<table>
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<th>Basis set</th>
<th>(R_o) (Å)</th>
<th>(V_o) (kcal/mol)</th>
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required. The calculations also suggest it will be a challenge to use \textit{ab initio} theory to calculate an accurate potential for CH\textsubscript{4} interacting with a Ni-atom cluster, representing a Ni surface. A complete potential will include both the CH\textsubscript{4}/Ni\{111\} physisorption interaction considered here and reaction pathways between CH\textsubscript{4} and the Ni surface.\textsuperscript{33} When a more accurate CH\textsubscript{4}−Ni(s) potential is developed, it will be of interest to use it in a trajectory simulation of Ar + CH\textsubscript{4}/Ni\{111\} CID.

\section*{ACKNOWLEDGMENTS}

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\item 32. J. T. Yardley, \textit{Introduction to Molecular Energy Transfer} (Academic, New York, 1980).
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