Observation of rotationally mediated focused inelastic resonances in D_2 scattering from Cu(001)

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Rotationally mediated focused inelastic resonances (RMFIR's) in the angular distributions of D_2 scattered from Cu(001) are observed. The FIR effect involves a phonon-assisted focusing of an incident beam of arbitrary energy and direction into a final channel of one single well-defined energy and direction. Surprisingly for an incident energy $E_i = 27$ meV the RMFIR conditions for the scattered beam coincide with the kinematic conditions required for a further elastic selective adsorption mechanism called the rotationally mediated critical kinematic (RMCK) effect. By taking advantage of the RMFIR and elastic RMCK effects, three effective bound states of energy $\epsilon_{n,J} = -21.5$ meV, -12.4 meV, and -10.3 meV are determined. They are attributed to the lowest bound states $\epsilon_0 = -28.9$ meV and $\epsilon_1 = -19.8$ meV combined with the rotational excitation energy for $J=1$ to be $B_{\text{rot}}J(J+1) = 7.41$ meV, respectively, and $\epsilon_3 = -10.3$ meV combined with the rotational ground state ($J=0$). While the ϵ_1 and ϵ_3 states appear as maxima in the angular distribution at RMFIR conditions, the ϵ_0 yields a striking minimum which represents the first evidence of what we call an anti-FIR feature. Theoretical arguments to explain the different FIR signatures observed are provided. A fit of a phenomenological interaction potential to the experimental bound-state values yields a value for the well depth $D = 32.5$ meV which is somewhat deeper than that found previously. [S0163-1829(97)00839-4]

I. INTRODUCTION

Recently, a mechanism for selective adsorption called focused inelastic resonance (FIR) has been theoretically predicted¹ for scattering of particles for which bound surface states exist. The enhancement of the selective adsorption process due to the FIR mechanism occurs when the following two conditions are met: (i) the scan curve (energy gain-loss versus parallel wave-vector transfer curve) and the inelastic resonance curve for a particular bound state are tangent to each other and (ii) this tangency point crosses the Rayleigh surface mode or any other active surface phonon mode. As opposed to the well known and extensively studied selective adsorption resonances the coupling into the bound state does not depend on the surface having a significant corrugation. The FIR effect was recently observed in angular distributions for scattering of He from the highly corrugated alkali halide surface of NaCl(001),² but until now no evidence of FIR has been reported for scattering from metal surfaces. In this work the FIR effect is observed in the angular distributions of D_2 scattered from Cu(001) but is mediated by the rotation of the molecule, the rotationally mediated focused inelastic resonance (RMFIR) effect. The analysis of the RMFIR peaks allows the direct determination of the two lowest-lying bound states of D_2 on Cu(001) which have not, to our knowledge, been previously observed. By combining these new bound states energies with those reported in a previous experiment³ all of the bound states for this system have been determined. A generalized Morse potential with three parameters was fitted to the experimental bound-state values to yield a well depth of $D = 32.5$ meV which is somewhat deeper than $D = 30.9$ meV obtained previously.³

Interestingly, the three RMFIR peaks display different intensities and two different signatures (maximum and minimum). Theoretical arguments within the close-coupling formalism are provided to explain this striking difference between the signatures of the FIR peaks. Moreover, for a narrow range of incident-beam energies the intensity of a RMFIR peak is anomalously high. This singular behavior can be explained if the final beam energy and the final polar angle fulfill the requirements for a further selective adsorption process. The kinematic requirements for this effect were very recently established⁴ and the effect is called *rotationally mediated critical kinematic* effect (RMCK). The elastic CK effect, which was originally predicted for atom-surface scattering,⁵ occurs when a stationary value of the resonance curve with respect to any scattering variable (incident energy or incident polar or azimuthal angle) equals the corresponding bound-state energy. If instead of atoms diatomic molecules are considered, the CK effect can be mediated by rotational excitation (RMCK).⁴ As far as we know, no experimental evidence of the elastic or inelastic (phonon-assisted) atomic CK effect has been reported until now. However, there is strong evidence for the occurrence of the RMCK effect⁶ in the scattering of D_2 from Cu(001) when the specular diffraction intensity is measured as a function of the incident energy.

II. EXPERIMENT

The high-resolution scattering apparatus has a fixed angle θ_{SD} between the incident θ_i and final scattering θ_f angles, which are simultaneously varied by rotating the crystal surface around an axis perpendicular to the scattering plane. The incident and final scattering angle satisfy the relation θ_i

+ $\theta_f = \theta_{SD}$, where $\theta_{SD} = 95.76^\circ$. The angular resolution of the scattering apparatus is about 0.3° .⁷

The n -D₂ beam was produced by a nozzle beam source.⁷ Due to the formation of clusters in the expansion of D₂ the source had to be operated at stagnation temperatures above 70 K and source pressures below 10 bar. The energy resolution of the D₂ beam under these conditions was about 15%. The concentration of dimers and trimers in the beam was estimated to be below 10%.⁸

At the low beam energies employed (≤ 30 meV) in this experiment the excited rotational states of the D₂ molecules in the incident beam can be safely ignored.⁹ Thus 67% of the molecules are in the ground $J=0$ state of ortho-D₂ and the remaining 33% in the ground $J=1$ state of para-D₂.

The measurements were carried out on a Cu crystal oriented to within 0.5° of the (001) surface and cleaned *in situ* by ion sputtering and annealing as described in Ref. 7. During the scattering experiments the surface was maintained at a temperature $T_s = 60$ K to minimize multiphonon scattering.

III. THEORY

A. Kinematics of the RMFIR effect

The kinematic equations governing the FIR effect derive from the kinematical conditions expressing the conservation of energy and parallel momentum in a one-phonon interaction. From these two conservation laws, the following equation is derived for the scan curve (SC) in the $(\hbar\omega_\nu(\Delta\mathbf{K}), \Delta\mathbf{K})$ plane:¹⁰

$$\hbar\omega_\nu(\Delta\mathbf{K}) = -E_i + E_i \left(\frac{\sin\theta_i}{\sin\theta_f} \right)^2 \frac{(\mathbf{K}_i + \Delta\mathbf{K}_\parallel)^2 + \Delta\mathbf{K}_\perp^2}{\mathbf{K}_i^2}, \quad (1)$$

where E_i is the energy of the incident molecular beam, $\mathbf{k}_i$ and $\mathbf{k}_f$ the incident and final wave vectors, $\Delta\mathbf{K}$ the parallel momentum transfer, and $\Delta\mathbf{K}_\parallel$ and $\Delta\mathbf{K}_\perp$ its components parallel and perpendicular to the scattering plane, respectively. The active phonon mode of the surface is represented by its wave vector $\Delta\mathbf{K}$ and its frequency ω_ν . Note that hereafter the energies are given as the square moduli of the wave vectors in units of $\hbar^2/2m$ with m the particle mass.

The kinematic condition for corrugation and rotationally mediated selective adsorption resonances in phonon inelastic planar scattering from a crystal surface is given by the energy-conservation law, here called the resonance curve (RC):

$$E_{N_z}(E_i, \theta_i) = E_i - (\mathbf{K}_i + \Delta\mathbf{K} + \mathbf{N}_\parallel)^2 - \mathbf{N}_\perp^2 + \hbar\omega_\nu(\Delta\mathbf{K}), \quad (2)$$

and where the incident resonance condition is given by

$$E_{N_z}(E_i, \theta_i) = -|\epsilon_{nJ}| = -|\epsilon_n| + B_{\text{rot}}J(J+1). \quad (3)$$

In Eq. (3) $|\epsilon_n|$ is the energy of the n th bound state in the laterally averaged potential, and in Eq. (2) $\mathbf{N} = (\mathbf{N}_\parallel, \mathbf{N}_\perp)$ is the surface reciprocal lattice vector involved in the resonance process with the bound state and $\mathbf{N}_\parallel$ and $\mathbf{N}_\perp$ are its components parallel and perpendicular to the scattering plane, respectively. The last term on the right-hand side of Eq. (3) is the rotational energy of a diatomic molecule in the J th rotational quantum level with rotational constant $B_{\text{rot}} = \hbar^2/2I$, I

being the moment of inertia. The assignment of the quantum numbers n and J associated with the values $|\epsilon_{nJ}|$ determined from the analysis of the RMFIR peaks is a delicate matter. In fact, the bound state values $|\epsilon_{nJ}|$ obtained in this way can be due either to molecules incident in the $J=0$ rotational state, or to molecules incident in the $J=1$ rotational state. In the case of $J=0$ the rotational energy contribution is exactly zero and $|\epsilon_n| = |\epsilon_{nJ}|$ according to Eq. (3). In the case of $J=1$ the bound state energies are shifted, and we obtain $|\epsilon_n| = |\epsilon_{nJ}| + 2B_{\text{rot}}$, that is a shift of 7.41 meV.¹¹ The presence of the rotational energy term in Eq. (3) constitutes the main difference with respect to the case of atomic FIR. We call this resonance *rotationally mediated focused inelastic resonance*, RMFIR. The energetic shifts due to the magnetic quantum number m_J associated with a rotational state J will be neglected in this discussion as well as possible changes in the value of I due to the proximity of the D₂ molecules to the surface.

Finally, the RMFIR effect can be stated in the form of a very simple kinematical condition. This kinematical condition can be obtained by equating Eqs. (1), (2), and (3) and their derivatives and it results in a particularly simple relation for the final scattering angle θ_f to be

$$\tan^2 \theta_f = \frac{|\epsilon_{nJ}| - \mathbf{N}^2}{\mathbf{N}_\parallel^2}. \quad (4)$$

The most important feature of Eq. (4) is that the final scattering angle does not depend on the incident energy and angle. Thus a peak corresponding to RMFIR conditions in an angular distribution should not change its angular position when the beam energy is varied. An important enhancement of the intensity of the RMFIR resonance is expected to occur when the tangency point coincides with a surface mode. The RMFIR locus in the dispersion space can be obtained by substitution of Eq. (4) into Eqs. (1), (2), and (3). For planar scattering this is written in a parametric form as a function of E_i as

$$\hbar\omega_\nu(\Delta\mathbf{K}) = -E_i + \frac{(|\epsilon_{nJ}| - \mathbf{N}^2)(|\epsilon_{nJ}| - \mathbf{N}_\perp^2)}{\mathbf{N}_\parallel^2} \quad (5)$$

and

$$\Delta\mathbf{K} = -E_i^{1/2} \sin\theta_i + \frac{(|\epsilon_{nJ}| - \mathbf{N}^2)}{N_\parallel}. \quad (6)$$

In this space, this locus is represented by the branch of a parabola and when this curve intersects a surface active phonon-dispersion curve, this effect is expected to be highly enhanced.

B. Kinematics of the inelastic and elastic RMCK effects

The kinematic equations governing the RMCK effect are easily deduced from Eqs. (2) and (3) and the condition $\partial E_{N_z}/\partial E_i = 0$ at constant θ_i . Thus we have that

$$|\epsilon_n| = (\Delta\mathbf{K} + \mathbf{N}_\parallel)^2 (1 + \tan^2 \theta_i) + \mathbf{N}_\perp^2 + B_{\text{rot}}J(J+1) - \hbar\omega_\nu(\Delta\mathbf{K}) \quad (7)$$

and the tangency condition occurs for an incident energy of

FIG. 1. A series of diffraction spectra of n -D₂ scattered from Cu(001) along the [100] direction at a surface temperature $T_s = 60$ K. The labels in parentheses refer to the elastic diffraction peaks. (00): specular elastic diffraction peak. (11) and (1 $\bar{1}$): first-order elastic diffraction peaks. F_1 , F_2 , and AF indicate RMFIR peaks and R refers to rotational inelastic diffraction peaks.

$$E_i = (\Delta \mathbf{K} + \mathbf{N}_{\parallel})^2 \frac{\sin^2 \theta_i}{\cos^4 \theta_i}. \quad (8)$$

Since the RC [Eq. (2)] is a very smooth function of E_i , the tangency condition can be nearly fulfilled for many points of this curve. When this is the case, a highly enhanced feature in the angular distribution is expected. Similar equations but in terms of the other scattering variables (polar or azimuthal angles) are also possible and have been reported in Refs. 4, 5.

Finally, Eqs. (7) and (8) can be reduced to no phonon exchange scattering if $\hbar \omega_\nu$ and $\Delta \mathbf{K}$ are set equal to zero,

$$|\epsilon_n| = \mathbf{N}_{\parallel}^2 (1 + \tan^2 \theta_i) + \mathbf{N}_{\perp}^2 + B_{\text{rot}} J(J+1) \quad (9)$$

and

$$E_i = \mathbf{N}_{\parallel}^2 \frac{\sin^2 \theta_i}{\cos^4 \theta_i}. \quad (10)$$

We will show in the following that the coincidence of RMFIR and elastic RMCK is a special feature of the D₂/Cu(001) scattering system.

C. Resonance signatures

In the CC formalism, any resonance profile (elastic or inelastic) can be expressed as⁵

$$\frac{|s_{\Delta \mathbf{K},0}|^2}{|s_{\Delta \mathbf{K},0}^{\text{bg}}|^2} = \left| 1 + i \frac{b_{\Delta \mathbf{K},0}}{x + i} \right|^2, \quad (11)$$

where $s_{\Delta \mathbf{K},0}$ and $s_{\Delta \mathbf{K},0}^{\text{bg}}$ are, respectively, the matrix elements of the scattering matrix and its background, between the specular channel and the $\Delta \mathbf{K}$ channel. The x variable represents a dimensionless deviation from the resonance position ($x=0$) and is defined by

$$x = \frac{2}{\Gamma_{nJ}} (E_{N_z} - \epsilon_{nJ}), \quad (12)$$

with Γ_{nJ} the width of the resonance and E_{N_z} the z component of the kinetic energy of the resonant channel $\mathbf{N}$ according to Eq. (2). Finally, $b_{\Delta \mathbf{K},0}$ is a complex number and is proportional to the ratio between the resonant and direct (or background) amplitudes evaluated at the resonance position,⁵

$$b_{\Delta \mathbf{K},0} = -2 \frac{(|r_{\Delta \mathbf{K},0}|/\Gamma_{nJ})e^{i\phi_r}}{|s_{\Delta \mathbf{K},0}^{\text{bg}}|e^{i\phi_{\text{bg}}}} = 2 \frac{|\bar{r}_{\Delta \mathbf{K},0}|}{|s_{\Delta \mathbf{K},0}^{\text{bg}}|} e^{i(\phi_r - \phi_{\text{bg}} + \pi)}, \quad (13)$$

where both amplitudes $\bar{r}_{\Delta \mathbf{K},0}$ and $s_{\Delta \mathbf{K},0}^{\text{bg}}$ are complex numbers. The second expression in Eq. (13) is more adequate for physical discussion since it involves only the three parameters needed to characterize the signature of a resonance, namely, the phase of the b parameter defined by $\phi = \phi_r - \phi_{\text{bg}} + \pi$ which includes the phase difference between both amplitudes, $|\bar{r}_{\Delta \mathbf{K},0}|$ the magnitude of the resonance amplitude divided by its width Γ_{nJ} , and $|s_{\Delta \mathbf{K},0}^{\text{bg}}|$ the magnitude of the direct or background amplitude.

Thus depending on $b_{\Delta \mathbf{K},0}$, the line shapes will present different signatures: (i) maximum or minimum Lorentzian-type profiles for real values and (ii) Fano-type profiles for complex values. According to Eq. (11) evaluated at the resonance position ($x=0$), it is clear that the b values $\{0, -1, -2\}$ have to be excluded because no peak would be reproduced (only the inelastic background for 0 and -2 or some unphysical process for -1). Now the following rules can be stated:

(i) If $\phi=0$ then $b_{\Delta \mathbf{K},0} \in]0, \infty[$ and according to Eq. (11) profiles will always exhibit a *maximum*.

(ii) If $\phi=\pi$ and $|\bar{r}_{\Delta \mathbf{K},0}| > |s_{\Delta \mathbf{K},0}^{\text{bg}}|$ then $b_{\Delta \mathbf{K},0} \in]-\infty, -2[$ and again profiles will have a *maximum*. If on the contrary $|\bar{r}_{\Delta \mathbf{K},0}| < |s_{\Delta \mathbf{K},0}^{\text{bg}}|$ then $b_{\Delta \mathbf{K},0} \in]-2, -1[\cup]-1, 0[$ and according to Eq. (11) profiles will exhibit a *minimum*.

(iii) If $\phi \neq 0$ or π then $b_{\Delta \mathbf{K},0}$ is a complex number and *Fano-type* profiles will always result.

It should be noticed that the x variable of Eq. (12) has a different expression depending on whether the kinematic conditions for the effects we have studied in the last two subsections are incorporated. If instead of the x variable other scattering variables (namely, the incident energy or some polar angle) are explicitly used under these special conditions the profiles given by Eq. (11) are no longer Lorentzian- or Fano-type functions as was shown elsewhere.^{5,1} The profiles are now replaced by

FIG. 2. Energy transfer vs parallel momentum-transfer plot for Cu(001) [100] showing the Rayleigh (RW) phonon-dispersion curve (Ref. 7), the resonance curve (RC), and the scan curve (SC). (a): SC and RC plotted for an incident energy $E_i = 27$ meV and an angle $\theta_f = 44.5^\circ$, corresponding to the F_1 peak in Fig. 1. (b): SC and RC plotted for an incident energy $E_i = 27$ meV and an angle $\theta_f = 57.3^\circ$, corresponding to the AF peak in Fig. 1. The horizontal scale is given in terms of multiples of the reciprocal-lattice vector $\mathbf{N}$ in the [100] direction.

$$\frac{|s_{\Delta\mathbf{K},0}|^2}{|s_{\Delta\mathbf{K},0}^{\text{bg}}|^2} = \left| 1 + i \frac{b_{\Delta\mathbf{K},0}}{x_q^2 + i} \right|^2, \quad (14)$$

where q stands for E_i or θ_i , $x_q = 2(q - \bar{q})/\Gamma_q$ with $\bar{q}$ and Γ_q the resonance position and the width observed in the q variable, respectively. Thus the rules for maxima and minima hold but the functional dependence is with x_q^4 not with x^2 . However, the maximum-minimum (or reverse) Fano profiles are replaced by profiles with two maxima or two minima.⁶

IV. RESULTS AND DISCUSSION

In Fig. 1 six angular distributions taken at energies between 16 and 36 meV are shown along the [100] azimuth of Cu(001) plotted as a function of the difference angle with respect to the specular peak $\Delta\theta = \theta_i - \theta_{\text{SD}}/2$. In these plots, the most prominent peaks correspond to the specular [$\mathbf{N} = (00)$] and to the second-order [$\mathbf{N} = (11)$ and $\mathbf{N} = (\bar{1}\bar{1})$] elastic diffraction peaks. The intensity of the specular peaks is about 5×10^5 counts per second. Other features marked by

F_1 , F_2 , and AF appear in Fig. 1 on each side of the specular peak as either a tiny minimum (AF) or two maxima (F_1, F_2) and are seen to always appear at the same angular position irrespective of the incident energy. The angular position of the minimum corresponds to a final scattering angle of $\theta_f = 57.3^\circ \pm 0.2^\circ$ (AF) and for the two maxima to $\theta_f = 44.5^\circ \pm 0.2^\circ$ (F_1) and $\theta_f = 38.6^\circ \pm 0.2^\circ$ (F_2). The AF and F_2 features seem to be spaced at the same positive and negative angles but this coincidence is purely by accident. These energy independent features are candidates for the RMFIR effect. In the last three spectra several maxima marked by R are due to the *rotational inelastic diffraction* process. The intensity and the number of the R peaks increases with incident energy and interferes with the RMFIR peaks. A more detailed discussion of the R peaks can be found elsewhere.¹² We will now concentrate our attention on the RMFIR peaks.

(i) F_1 and F_2 maxima. By using Eq. (4) with the values $\theta_f = 44.5^\circ$ (F_1) and $\theta_f = 38.6^\circ$ (F_2), $\mathbf{N}^2 = \mathbf{N}_{\parallel}^2 = 6.287$ meV we obtain for the two bound states the following values: $|\epsilon_{11}| = 12.4 \pm 0.2$ meV and $|\epsilon_{30}| = 10.3 \pm 0.2$ meV. To confirm the assignment to a RMFIR peak, in Fig. 2(a) we plot in the $[\hbar\omega_v(\Delta\mathbf{K}), \Delta\mathbf{K}]$ plane the following four curves: RC [Eq. (2)] and SC [Eq. (1)] for an incident energy of $E_i = 27$ meV and a scattering angle $\theta_f = 44.5^\circ$ (resonance F_1), together with the surface Rayleigh (RW) dispersion curve as given in Ref. 7. As can be seen, the tangency condition required for the RMFIR effect is fulfilled in the *creation* region. Under such conditions, $E_i > E_f$ and the unscattered waves emerge from the scattering region *ahead* of the scattered waves. According to the rules stated in Sec. III C in connection with Eq. (13), a maximum can occur when a phase difference of π exists between the unscattered and scattered amplitudes. Since the resonances appear as maxima in the angular distributions, the incident flux passes mostly through the resonance pathway and the probability of the resonance process is greater than the probability of the direct process.

(ii) AF minimum. Only one AF minimum is observed for a scattering angle of $\theta_f = 57.3^\circ \pm 0.2^\circ$. By using Eq. (4) with the same values of the reciprocal-lattice vector we obtain a value for the bound state $|\epsilon_{01}| = 21.5 \pm 0.2$ meV. In Fig. 2(b) the same curves as in Fig. 2(a) are shown but here the RC and SC curves are plotted for $E_i = 27$ meV and $\theta_f = 57.3^\circ$. Notice that now the tangency condition required for the RMFIR effect is fulfilled in the *annihilation* region. We designate this minimum as an anti-RMFIR effect. Under these conditions again a phase change of π is expected between the incident and the scattered amplitudes but opposite to the RMFIR conditions the presence of a minimum indicates that the probability of the resonance process is less than the probability of the direct process.

Figure 1 shows the unusually large intensity displayed by the F_1 maximum compared to the other RMFIR peaks. The enhancement of the F_1 intensity is particularly evident when the incident energy is $E_i = 27$ meV. A closer examination of the kinematics at these conditions reveals the presence of the elastic RMCK effect at 27 meV. In fact, if we substitute the values $E_i = 27$ meV and $\theta_f = 44.5^\circ$ in Eq. (5) we get $\hbar\omega_v = -14.94$ meV and $E_f = 12.1$ meV. If these data of the final polar angle and final energy are included in Eqs. (9) and (10) where the subindex i is replaced by f , then we get $|\epsilon_{11}|$

FIG. 3. The elastic resonance curve after Eq. (2) is plotted as a function of the incident energy for a polar angle of $\theta_i = 44.5^\circ$ together with the bound state $|\epsilon_{nJ}| = 12.4$ meV, represented by a horizontal line. The tangency point is at $E_i = 12.1$ meV.

$= 12.4$ meV which is exactly the same value for the bound state obtained from the analysis of the F_1 resonance peak. So, the physical picture of the resonance F_1 at $E_i = 27$ meV is the following. The incident molecules satisfy the kinematical conditions for the RMFIR effect. This is a phonon *inelastic* effect, and the projectiles lose $\hbar\omega_v = 14.94$ meV of their energy. Their final energy, $E_f = 12.1$ meV, satisfies the conditions of the RMCK resonance, which enhances further the intensity of the F_1 peak. Figure 3 illustrates the kinematic conditions of the elastic RMCK effect. The RC from Eq. (2) is plotted as a function of the incident energy in the range covered by the experimental conditions with $\hbar\omega_v = 0$ and $\Delta\mathbf{K} = 0$ together with an horizontal line representing the bound state $|\epsilon_{nJ}| = 12.4$ meV. The tangency point at $E_i = 12.1$ meV corresponds to the final energy of the molecules after the RMFIR process. Furthermore, the curve is very smooth around the tangency point and a small range of energies around 12.1 meV will also contribute to enhance the elastic resonance process which explains why the F_1 peak is as a rule more intense than the remaining RMFIR peaks. Thus an inelastic resonance process (RMFIR) provides the conditions for a subsequent resonance elastic process through the RMCK mechanism.

In Table I we report the assigned values of ϵ_n together with the data reported by Andersson, Wilzen, and Persson³ from an experimental study of corrugation-mediated selective adsorption resonances for this system. Similar values of the bound states labeled by $n = 4, 5$, and 6 were also measured in the past for the scattering of D_2 from Cu(111).¹³ In our assignment we assumed that the value $\epsilon_{nJ} = -21.5$ meV corresponds to the bound state $n = 0$ for molecules in the $J = 1$ state, the value $\epsilon_{nJ} = -12.4$ meV corresponds to the bound state $n = 1$ for molecules in the $J = 1$ state, and the value $\epsilon_{nJ} = -10.3$ meV to the bound state $n = 3$ for molecules in the $J = 0$ state. In Table I we also list the theoretical values fitting the experimental values when

TABLE I. Comparison of bound-state energy levels ϵ_n of D_2 on Cu(001). The second column shows the values ϵ_n measured in this work at RMFIR conditions, the third column lists the values determined by Andersson, Wilzen, and Persson (Ref. 3), and the fourth one the theoretical values obtained from the potential given in Eq. (15) with the following fitting parameters: $D = 32.5$ meV, $\lambda = 1.09 \text{ \AA}^{-1}$, and $p = 4.5$.

n	Present Expt.	Andersson <i>et al.</i>	Fitted values
0	-28.9 ± 0.2	-27.3^a	-28.2
1	-19.8 ± 0.2	-20.4^a	-20.7
2		-14.5 ± 0.2	-14.8
3	-10.3 ± 0.2	-10.3 ± 0.2	-10.1
4		-6.7 ± 0.2	-6.6
5		-4.3 ± 0.2	-4.0
6		-2.6 ± 0.2	-2.2
7		-1.2 ± 0.2	-1.0

^aDetermined in Ref. 3 by fitting a model potential to the experimental values.

the phenomenological potential originally proposed by Mattera *et al.*¹⁴ is used. This variable exponent potential is a three parameter generalization of the Morse potential which has been successfully used for fitting atom/molecule-surface interactions,

$$V(z) = D[(1 + \lambda z/p)^{-2p} - 2(1 + \lambda z/p)^{-p}], \quad (15)$$

where z is the distance from the center of mass of the molecule to the surface and D is the well depth; λ is a positive parameter and p a parameter such that $-1 \leq 1/p \leq 1$ which controls the width and the symmetry of the potential. Equation (15) has the advantage that its bound states can be derived from an approximate analytical function given by

$$\epsilon_n = -D[(1 + \delta/A^2)^{-1/5} - (n + 1/2)/As]^s, \quad (16)$$

FIG. 4. The generalized Morse potential together with its eight bound states (solid lines) given by Eqs. (15) and (16), respectively, for the interaction of D_2 with Cu(001). The following parameter has been used: $D = 32.5$ meV, $\lambda = 1.09 \text{ \AA}^{-1}$, and $p = 4.5$. Dashed lines correspond to the experimental energy values.

where $\delta = (1 + 1/p)/32p$, $A = (2mD)^{1/2}/2\hbar\lambda$, and $1/s = 1/2 - (1/4p)(3 + 1/p)$. The best-fit parameters are $D = 32.5$ meV, $\lambda = 1.09 \text{ \AA}^{-1}$, and $p = 4.5$ which yield values of the bound states within 5% of the experimental values. In Fig. 4 a plot of this interaction potential together with the experimental and fitted bound states is presented.

In conclusion the analysis of the RMFIR peaks allows the direct experimental determination of the two lowest ($n = 0, 1$) bound states of the physisorption potential of D_2 on the very smooth Cu(001) surface. The FIR effect makes it possible to access bound states of the physisorption potential which because of the small diffraction intensities could not be accessed with other experimental methods such as selective adsorption. Furthermore the first observation of the elas-

tic RMCK combined with the RMFIR effect is reported. This singular behavior displayed by this system at certain incident energies could be exploited to enhance chemical reaction on metal surfaces.

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¹G. Benedek and S. Miret-Artés, *Surf. Sci.* **339**, L935 (1996).

²G. Benedek, R. Gerlach, A. Glebov, G. Lange, S. Miret-Artés, J. G. Skofronick, and J. P. Toennies, *Phys. Rev. B* **53**, 11 211 (1996).

³S. Andersson, L. Wilzen, and M. Persson, *Phys. Rev. B* **38**, 2967 (1988).

⁴S. Miret-Artés, *Surf. Sci.* **366**, L735 (1996).

⁵M. Hernández, S. Miret-Artés, P. Villarreal, and G. Delgado-Barrio, *Surf. Sci.* **251/252**, 369 (1991); **274**, 21 (1992); S. Miret-Artés, *ibid.* **294**, 141 (1993).

⁶M. F. Bertino, S. Miret-Artés, and J. P. Toennies (unpublished).

⁷F. Hofmann, J. R. Manson, and J. P. Toennies, *J. Chem. Phys.* **101**, 10 155 (1994).

⁸D. R. Miller, in *Atomic and Molecular Beam Methods*, edited by

G. Scoles (Oxford University Press, New York, 1988), pp. 14–53.

⁹K. Kern, R. David, and G. Comsa, *J. Chem. Phys.* **82**, 5673 (1985).

¹⁰G. Benedek, G. Brusdeylins, J. P. Toennies, and R. B. Doak, *Phys. Rev. B* **27**, 2488 (1985).

¹¹K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1978), Vol. IV.

¹²M. F. Bertino, F. Hofmann, and J. P. Toennies (unpublished).

¹³U. Harten, J. P. Toennies, and Ch. Wöll, *J. Chem. Phys.* **85**, 2249 (1986).

¹⁴L. Mattera, C. Salvo, S. Terreni, and F. Tommasini, *Surf. Sci.* **97**, 158 (1980); M. Chiesa, L. Mattera, R. Musenich, and C. Salvo, *ibid.* **151**, L145 (1985).