

accurate focusing, a necessary feature for strongly refracting media, and that it is relatively unaffected by harmonic emission from the plasma.

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Theoretical Analysis of Bound-State Resonance Data in He-LiF Scattering

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The He-LiF selective-adsorption data of Frankl and co-workers are analyzed using an attractive-well, corrugated-wall model. The model is solved to convergence by an expansion method. The calculated He-LiF spectrum is in good agreement with experiment. Calculations show that the intensity of weakly bound states is enhanced by band splitting with stronger resonances. This may provide a method for observing these states.

Recently there has been a great deal of experimental and theoretical interest in the scattering of He beams from solid surfaces. For systems such as LiF at low surface temperatures, the scattering features are predominantly elastic (diffractive). At sufficiently low beam energies or large incident angles the elastic intensity is dominated by contributions from combined state resonances in the attractive surface-averaged potential $V_{00}(z)$. These resonances are commonly known as selective adsorptions. As is well known they lead to a rather detailed knowledge of the bound states of $V_{00}(z)$.

In this article, we discuss the selective adsorption data of Frankl and co-workers¹ by introducing an attractive-well, corrugated-wall model of atom-surface scattering. The solution to the model utilizes a Rayleigh expansion.² The resulting matrix equation is solved as a series expansion. The theory is applied to the He-LiF system, and is shown to be in good agreement with experiment. The method provides an inexpensive means to parametrize surface potentials and explain complex regions in the experimental data.

As has become apparent from a wide range of investigations,³ the atom-surface potential may be characterized by a short-ranged strongly repulsive region and a long-ranged weakly attractive region. With these features in mind we use a model potential defined as

$$V(X, z) = \begin{cases} \infty, & z > \epsilon\sigma(X), \\ V_a(z), & z < \epsilon\sigma(X). \end{cases} \quad (1)$$

z is normal to the surface and $X = (x, y)$. $V_a(z)$ is general and is used to fit the experimental data. Square-well attractive potentials with the corrugated wall have been investigated by other authors.⁴ $\sigma(X)$ is a periodic function with the periodicity of the surface. ϵ is the coupling parameter representing the strength of periodicity of the surface. For the purposes of this Letter $\sigma(X)$ will be taken as $\cos(2\pi x/\alpha) + \cos(2\pi y/\alpha)$, although higher Fourier terms may be included with little difficulty. The parameter α is the lattice spacing on the surface.

By use of the Rayleigh hypothesis the total wave function is expanded in the series

$$\psi_{k_0, K}(X, z) = \varphi_{k_0}^{(-)} e^{iK \cdot X} - \sum_G B_G \varphi_{k_G}^{(+)} e^{i(K+G) \cdot X}. \quad (2)$$

K is the parallel translational wave vector (k_x, k_y) , and G is a reciprocal lattice vector $(2\pi n/\alpha, 2\pi m/\alpha)$. k_G , the perpendicular wave vector for channel G , is given by the usual conservation of energy relation. The functions $\varphi_{k_G}^{(\pm)}(z)$ are the solutions to the one-dimensional Schrödinger equation for $V_a(z)$, having $\exp(\pm ik_G z)$ asymptotic behavior for open channels and $\exp(\mp |k_G| z)$ behavior for closed channels. The transition probability to a given open diffractive channel G is proportional to $|B_G|^2$. The wave function in Eq. (2) must vanish at the infinite barrier [when $z = \epsilon\sigma(X)$ in Eq. (1)]. This boundary condition gives the following matrix equation for the scattering amplitudes, B_G :

$$\sum_{G'} A_{G, G'}^{(+)}(\epsilon) B_{G'}(\epsilon) = A_{G, 0}^{(-)}(\epsilon), \quad (3)$$

where

$$A_{G',G}^{(*)}(\epsilon) = \langle G' | \psi_{k_G}^{(*)}(\epsilon \sigma(X)) | G \rangle.$$

We wish to develop a series solution for B_G . An expansion of $A_{G',G}^{(*)}$ in powers of the roughness parameter, ϵ , results in the series

$$A_{G',G}^{(*)}(\epsilon) = \sum_{n=0}^{\infty} \frac{\epsilon^n}{n!} \left(\frac{\partial^n \psi_{k_G}^{(*)}}{\partial z^n} \right)_{z=z_0} \langle G' | \sigma(X)^n | G \rangle. \quad (4)$$

If we treat ϵ as a small expansion parameter (the validity of this will be demonstrated by the numerical convergence of the method), then the zeroth-order approximation to Eq. (3) will correspond to the scattering from a potential which is infinite at z_0 and attractive for $z > z_0$. Bound states, E_b^z , for this zeroth-order potential exist when $\varphi_{k_G}^{(*)}(z_0) = 0$ for $k_G^2 < 0$. The total energy of this solution may be greater than zero because of the translational energy in the plane of the surface. A direct expansion of the scattering amplitudes in powers of ϵ will result in division by $\varphi_{k_G}^{(*)}(z_0)$, and will therefore diverge when any k_G is near a bound state. This result is analogous

to the difficulties incurred in the Born series when a bound state overlaps the continuum. We remove these bound-state divergence problems by using projection-operator techniques. This method has a distorted-wave perturbative analog developed to treat resonances in nuclear physics.^{5,6} While this method is not a perturbation expansion in a weak potential, its convergence is closely related to the convergence of the analogous distorted-wave theory for such interactions.⁷ Usually, high-order calculations with such theories are computationally impractical. Because of the choice of potential in Eq. (1) higher-order calculations are possible here. This appears to be the fastest way to solve for the scattering amplitudes for our choice of potential and incident perpendicular wave vector, k_0 . Defining an operator, Q , which projects onto those channels which have a k_G approximately equal to that of a bound state of the zeroth-order potential (resonant channels), and its orthogonal complement P , we may partition the matrix equation, Eq. (3), and solve for the vector $B_P = PB$. B_P contains all the open-channel and nonresonant closed-channel scattering amplitudes. We obtain

$$B_P = A_{PP}^{-1} A_P^{(-)} - (A_{FP}^{-1} A_{PQ}) \cdot (A_{QQ} - A_{QP} A_{PP}^{-1} A_{PQ})^{-1} \cdot (A_Q^{(-)} - A_{QP} A_{FP}^{-1} A_P^{(-)}). \quad (5)$$

The matrices in Eq. (5) are defined analogously to B_P [e.g., $A_{QP} = QA^{(+)}P$, where $A_P^{(-)}$ is the projection of the right-hand side of Eq. (3)], A_{FP}^{-1} may be expanded in ϵ . The first term in Eq. (5) is the direct scattering. Strong resonance features in the scattered intensity (selective adsorptions) appear when contributions from the second term in Eq. (5) becomes large. This occurs when the determinant of

$$W = (A_{QQ} - A_{QP} A_{FP}^{-1} A_{PQ}) \quad (6)$$

is nearly zero. W is a function of the incident energy, E . The approximate positions of the selective adsorptions are given by the zeros in the uncoupled limit of $\det|W|$. These satisfy the Lennard-Jones-Devonshire equation

$$E = E_b^z + (\hbar^2/2m)(K + G)^2 \quad (7)$$

for a given combination of bound state and reciprocal lattice vector, denoted by $b(n, m)$. For $\epsilon > 0$, the complex E for which $\det|W|$ vanishes is shifted from the energy given by Eq. (7). The real part of this shift, when added to E_b^z of Eq. (7), gives the position of the resonance. The imaginary part gives its width.

In Fig. 1 we compare calculations using Eq. (5) with the experiments of Meyers and Frankl.¹

$V_a(z)$ is a 12-3 type potential and ϵ is taken to be 0.15 Å, the value chosen to fit high-energy scattering data.⁸ The uncoupled bound states were initially fitted to those of Meyers and Frankl,¹ followed by adjustments in potential parameters until the calculated first-order minima agreed with experiment. Calculations were carried to numerical convergence of about three significant figures (≤ 10 th order). The bound states arrived at in this way were -6.1, -2.5, -0.8, -0.2, and -0.03.

With the exception of E_0^z and E_4^z all the bound-state energies were in excellent agreement with the newest bound states derived from experiment by Derry *et al.*¹ using Eq. (7). These authors report $E_0^z = -5.90$ and observe no fifth bound state. The discrepancy in E_0^z , the deepest bound state, is caused by a shift due to coupling to the continuum. In Fig. 1 the vertical lines represent solutions to Eq. (7). The resonance minimum for the 0(0, 1) bound state occurs near $\varphi = 25^\circ$. If E_0^z was computed from the position of this minimum using Eq. (7), it would be found to be that of Derry *et al.*¹ In this case the 0(0, 1) was separate from overlapping resonances.

In Fig. 1 near $\varphi = 35^\circ$ three peaks are observed

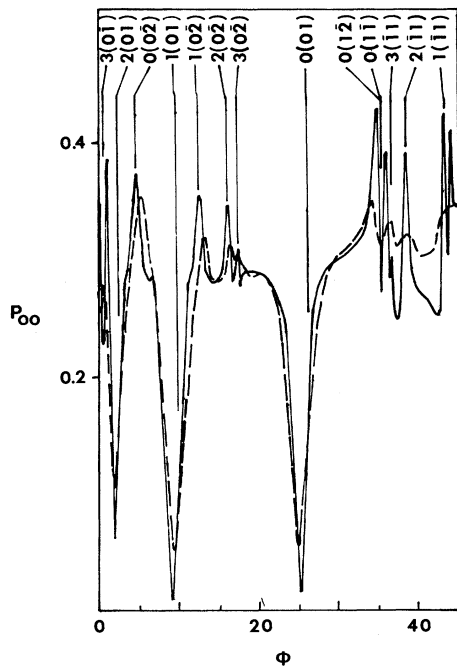


FIG. 1. Comparison of attractive-well, corrugated-wall theory (solid line) versus experiment (dashed line) for $\lambda = 1.03 \text{ \AA}$, $\theta = 70^\circ$.

experimentally. Although the middle peak might be labeled as the $3(-1, 1)$ resonance, our calculations show that the majority of the middle peak's amplitude comes from one of the band-split⁹ states of the degenerate $0(1, -1)$ and $0(1, -2)$. Although the $0(1, -2)$ is not normally observed, it splits the $0(1, -1)$ in first order, and "borrows" intensity from the more strongly resonant state.

The borrowing of intensity from strongly resonant peaks to enhance weak processes may provide a means for measuring energies of weakly bound states. In Fig. 2 the solid vertical line indicates where the $4(-1, 1)$ and the $0(0, 1)$ states are degenerate. Two peaks separated by 1° are observed because of the presence of the fifth bound state in our potential. Although the existence of a fifth bound state for He-LiF is speculative, experiments of this kind may be able to detect its presence. Careful calculations show that the $4(0, 1)$ resonance has a width less than 0.1 deg . While a 0.1-deg resonance is not resolvable on existing apparatus,¹⁰ the structure in Fig. 2 might be resolved. The existence and energy of a fifth bound state has important consequences in determining the van der Waals coefficient, C_3 , from experiment.¹¹

The attractive-well, corrugated-wall is a good model for elastic atom-surface scattering of He-

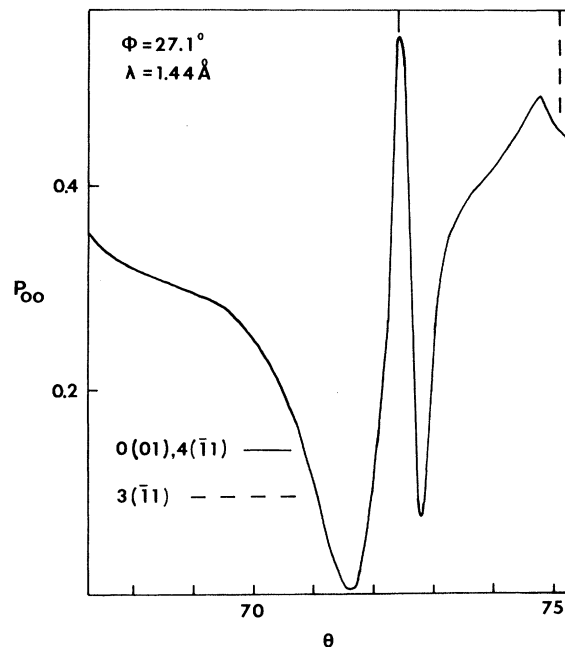


FIG. 2. The splitting of the $0(0, 1)$ by a fifth bound state. Vertical solid and dashed lines indicate the expected resonance position predicted by Eq. (7).

LiF. The substantial agreement with experiment in Fig. 1 over a wide range of angles is impressive. Estimates from Eq. (7) indicate that this agreement will not be significantly altered by energy or angle averaging. Similar agreement is obtained for other incident scattering angles. The adjustable parameters C_3 , z_0 , and the potential depth were used to fit the bound states. The agreement with experiment has been obtained without the explicit inclusion of a $(1, 1)$ Fourier component in the corrugation equation for $\sigma(X)$, Eq. (1). Recent perturbation calculations⁶ have shown that minima in scattering intensity for a particular $b(n, m)$ correlate with strong contribution from the (n, m) Fourier component in the potential. The experimental data in Fig. 1 exhibit maxima for the $(1, 1)$ resonances. The pairwise potential summation approximation of Chow and Thompson⁹ for He-LiF yields a large $V_{11}(z)$ component. Our results would indicate that such a potential cannot fit the data in the $30\text{--}45^\circ$ range.

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Electron Capture into the Two-Electron O^- State in GaP

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A reinterpretation of the ir spectra of Dean and Henry in oxygen-doped GaP strongly suggests that they involve radiative capture and excitation of the *second* electron bound to oxygen. Further, this electron is localized near the nearest-neighbor Ga ions, it is bound by ~ 0.9 eV as found also by Samuelson and Monemar, and its electron-phonon coupling is *small*— $\lambda \approx 0.6$, $\hbar\omega \approx 47.5$ meV—in disagreement with Henry *et al.* The analysis emphasizes the usefulness of the “phonon signature” in identifying deep levels from their optical spectra.

Dean and Henry (DH) have published a careful study of radiative electron capture onto deep oxygen donors in GaP.¹ Subsequently Henry and co-workers²⁻³ discovered by photocapacitance techniques that each oxygen donor in GaP could bind a second electron to become O^- , with each electron bound by nearly 1 eV. Since this latter discovery both states have been studied extensively, and two conflicting models for the two-electron state have developed—that of Henry and co-workers²⁻⁴ and that of Grimmeiss *et al.*⁵ and of Morgan.⁶ The former authors conclude that a very strong electron-lattice interaction is acting and, indeed, that GaP:O is a prime example of such interactions in semiconductors.⁴ The latter authors conclude that a kind of selection rule must be operating, so that optical transitions between the X_1 conduction-band edge and the two-electron ground state of O^- are very weak. In this Letter I reexamine the DH data and propose that they involve the *second* electron in O^- and allow important properties of this anomalous state to be determined.

An indication that the original one-electron interpretation of the DH data is incorrect is given by a comparison of the shape of the phonon replica structure in the luminescence spectrum of DH with that of the donor-acceptor (D-A) pair spectra of Dean, Henry, and Frosch,⁷ both of

which are shown in Fig. 1. Monemar and Samuelson have recently found⁸ that the same phonon energies [$\hbar\omega_1 = 19$ meV and $\hbar\omega_2 = 48$ meV (see also Ref. 7)] and relatively large coupling strengths [$\lambda_1 = 1.65$ and $\lambda_2 = 1.1$] which fit the pair (emission) spectra also explain the shape and temperature dependence of the photoneutralization (absorption) spectra for the O^0 ground state. [These are referred to as the configuration-coordinate (C-C) modes.] These phonons do *not* appear in other D-A pair spectra. Thus, this satellite structure may be considered the “signature” of the deep O^0 ground state with respect to its one-electron transitions.

The spectra in DH, however, are very different—in part because the zero-phonon transition O_0 (see Fig. 1) is forbidden and cooperation of a nonsymmetric (active) phonon is needed to relax the selection rule and produce a strong replica, and in part because the states are different. If the deep electron states involved in both of these spectra were the same, the C-C phonons and coupling strengths would be nearly the same (being only weakly dependent on the shallow state involved), and the same replicas of *any* strong features which appear in one spectrum would appear in both. Thus there would appear in Fig. 1(a) a strong broad 19-meV replica of O_{1oc}' and also of O_{TA} and of the optical phonon peaks, none of