

## CALCULATION OF ROTATIONALLY MEDIATED SELECTIVE ADSORPTION IN MOLECULE SURFACE SCATTERING: HD ON Pt(111)\*

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Rotationally mediated selective adsorption of HD on Pt(111) is examined theoretically using *R*-matrix scattering techniques. With a laterally averaged surface-molecule Morse potential interaction and for an anisotropic potential term transformed from H<sub>2</sub>, excellent agreement is obtained between the resonances and the first-order perturbed bound vibration-free rigid rotor energies.

The recent observation of sharp resonances (rotationally mediated selective adsorption) in the elastic and rotationally inelastic scattering of HD ( $J=0$ ) from heated Pt(111) surfaces [1] provides an excellent opportunity to determine the potential in this system. Selective adsorption is well known for atom-surface scattering [2], where it allows for the direct determination of the bound levels of the laterally averaged interaction potential. For molecule-surface scattering, the rotation of the molecule is an additional complication, but data from the rotationally inelastic scattering resonances permit us to determine whether or not there is substantial interaction between the rotational and translational motions in the quasi-bound state.

Several quantum-mechanical studies of atom-surface scattering have been extended to deal with collisions of diatomic molecules (H<sub>2</sub>, D<sub>2</sub>, HD) with corrugated surfaces [3], focusing mainly on the diffraction. In the HD-Pt(111) system rotationally inelastic scattering dominates [1], providing an ideal system in which to study the rotation-translation interactions.

For the HD-Pt(111) system we have done preliminary quantum-mechanical calculations aimed at explaining the experimentally observed transition probabilities and investigating the nature of the molecule-surface bound states. The Wigner ( $L^2$ ) *R*-matrix scattering method was used, since it gives a clear picture of the bound-state structure and a reasonably quantitative description of the scattering, despite the well-known problems of convergence [4].

Treating the molecule as a rigid rotor and neglecting diffraction allows us to use a potential which is a function only of  $z$ , the perpendicular distance from the surface to the molecule (c.m.), and  $\theta$ , the polar angle of the molecular axis from the normal to the surface. The hamiltonian then becomes

$$H = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2I} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + V(z, \theta). \quad (1)$$

(The azimuthal rotational quantum number,  $m$ , is conserved.)

We obtained the potential for HD by transforming the form commonly used for symmetric rotor-surface scattering to the new c.m. coordinate system:

$$V(z', \theta) = V_0(z') [1 + \beta P_2(\cos \theta)] \\ = V_0(z) + \sum_{l=0}^{\infty} u_l(z) P_l(\cos \theta), \quad (2)$$

where  $z'$  is the normal distance from the surface to the

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geometric centre of HD. If a Morse potential is used for  $V_0(z')$ , the first Legendre coefficient of the transformed potential is equal to the same Morse potential in  $z$ ,  $V_0(z)$ , plus a small correction term  $u_0(z)$ . We separate these to obtain the decoupled zeroth-order hamiltonian

$$H^0 = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2I} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + V_0(z), \quad (3)$$

whose eigenfunctions are products of Morse eigenfunctions and spherical harmonics. For the bound Morse states, these eigenfunctions will be referred to as the BVRR (bound vibration—rigid rotor) states.

A value of  $\beta = -0.24$  [3] was used and the experimentally determined well depth of 55 meV [1] was used for the Morse potential. The range parameter,  $\alpha = 0.4999 a_0^{-1}$ , was chosen such that the bound levels would fit those estimated experimentally for HD as a rigid rotor on Pt(111) [1]: this value gives a rms deviation of 1.36 meV and predicts three levels not observed experimentally, the two lowest and the uppermost. A major question to answer is whether the energies of the BVRR states so obtained are good estimates of the resonance states obtained in the full scattering calculation, which include the vibration—rotation coupling.

The  $R$ -matrix calculation used a basis of the direct product of free rotor states and the translational basis used to find the bound vibrational states. Sine functions were used for the translational basis. A total of 60 translational  $\times$  6 rotational = 360 states were employed.

Fig. 1 shows the calculated rotational transition probability for  $J = 0 \rightarrow 1$  as a function of the  $z$  component of the translational energy [the total scattering energy in eq. (1)] at a total translational energy of 109 meV (corresponding to the experimental beam energy). The positions of the sharp dips for all transition probabilities from  $J = 0$  and complementary peaks,  $E^c$ , are given in table 1, together with the BVRR energies,  $E^A$  are the energies of the BVRR states with the vibrational energy given by the analytic Morse eigenvalues. They are shown here for comparison with  $E^0$ , which is the BVRR energy with the vibrational energy calculated by diagonalization within the finite  $R$ -matrix translational basis. The differences are within 1.1 meV.  $E^1$  contains the diagonal portion of the vibration—rotation coupling in the BVRR basis in addition to  $E^0$ , i.e. it is the first-order corrected energy. The first-order correc-

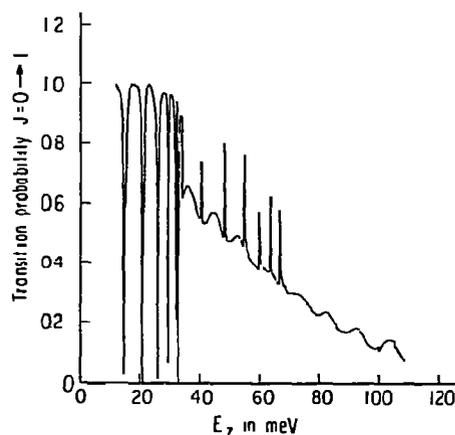


Fig. 1.  $J = 0 \rightarrow 1$  transition probability versus normal incident energy,  $E_z$  ( $E_z = E \cos^2 \theta$ ). The total energy  $E$  is 109 meV.

tions vary between 1.1 and 3.8 meV, increasing as  $N$ , the Morse quantum number, decreases, for a given  $J$ . The minima and complementary peaks of the scattering agree remarkably well with the first-order corrected BVRR energies,  $E^1$ . The level shift due to the first-order term is responsible for the variation in bound-level estimates in ref. [1]. The resonance structure becomes narrower with increasing  $J$ , and a slight deviation of  $E^c$  from  $E^1$  occurs at lower bound vibrational states for all  $J$  (table 1).

The  $J + 1$  resonances perturb the  $0 \rightarrow J$  transitions most strongly, causing deep minima: smaller complementary peaks occur in  $0 \rightarrow J - 1$  transitions and very small perturbations may be observed in  $0 \rightarrow J - 2$ . These effects are clearly seen in fig. 1, where the deep minima at low energies are the result of  $J = 2$  resonances, the smaller maxima between 40 and 70 meV are due to  $J = 3$  resonances, and the very small perturbations above 70 meV, just discernible in fig. 1, are due to  $J = 4$  resonances. The conclusion is that  $J + 1$  resonance states decay primarily to states other than the nearest open channel ( $J$ ), but the reason for this is not immediately clear. It may be merely a result of the relative sizes of  $u_1(z)$  and  $u_2(z)$ , the latter being larger in the attractive region and resulting in greater coupling from  $J + 1$  bound states to the  $J - 1$  final state, than from  $J + 1$  to  $J$ . The very small effect of  $J + 1$  resonances on  $0 \rightarrow J - 2$  transitions in comparison to  $0 \rightarrow J$  and  $0 \rightarrow J - 1$  would be consistent with this, since the direct coupling by  $u_3(z)$  is of short range.

Table 1

Comparison of calculated resonance energies with bound vibration-rigid rotor (BVRR) energies.  $N, J$  indexes the BVRR state  $N = 1, \dots, 8, J = 1, \dots, 4$ .  $E^A$  is the analytic BVRR energy,  $E^0$  is the BVRR energy with vibrational eigenvalues from the finite  $R$ -matrix translational basis  $E^1$  is  $E^0$  plus the first-order perturbation energy.  $E^C$  is the scattering resonance energy: maxima are labeled with an asterisk, minima have no label. All energies are in meV

$N, J$	$E^A$	$E^0$	$E^1$	$E^C$			
				$0 \rightarrow 3$	$0 \rightarrow 2$	$0 \rightarrow 1$	$0 \rightarrow 0$
7,4	108.1	107.4	108.6	108.6	108.6*	108.5*	108.6*
6,4	103.8	103.3	104.9	105.1	105.1*	105.0*	105.0*
5,4	98.3	97.6	99.7	99.9	99.9*	99.8*	99.8*
4,4	91.6	90.6	93.2	93.4	93.4*	93.3*	93.3*
3,4	83.7	82.6	85.5	85.8	85.8*	85.7*	85.7*
2,4	74.5	74.1	77.3	77.6	77.6*		77.6*
1,4	64.1	64.0	67.5		68.0*	68.1*	68.1
8,3	65.7	65.2	66.3		66.6	66.6*	66.6*
7,3	62.7	62.0	63.2		63.3	63.3*	63.3*
6,3	58.5	57.9	59.6		59.8	59.7*	59.8*
5,3	53.0	52.3	54.4		54.6	54.6*	54.6*
4,3	46.3	45.3	47.9		48.1	48.1*	48.2*
3,3	38.3	37.2	40.2		40.5	40.4*	40.5*
2,3	29.1	28.7	32.0			32.3*(33.7*)	32.3(33.7)
1,3	18.7	18.6	22.3				
8,2	31.7	31.1	32.4			32.9(32.2)	32.9*(32.2*)
7,2	28.7	28.0	29.3			29.4	29.4*
6,2	24.5	23.9	25.7			26.0	26.0*
5,2	19.0	18.2	20.5			20.9	20.9*
4,2	12.3	11.3	14.0			14.6	14.6*
3,2	4.3	3.2	6.4				

The two lowest bound states cannot be detected by such "nearest-neighbor" interactions at this total energy, although  $J+1$  resonances in these states do affect the  $0 \rightarrow J-1$  probabilities. An interesting feature is seen at 32 meV, where two resonant states ( $N=2, J=3$ ) and ( $N=8, J=2$ ) are nearly isoenergetic in  $E^1$ . For the  $0 \rightarrow 1$  transition, the  $J=2$  resonance should produce a minimum and the  $J=3$  resonance a maximum. Interference causes a splitting of both features to give the two closely spaced minima and two maxima visible in fig. 1 at  $\approx 32$  meV. This is referred to in table 1 by the entries followed by a second, bracketed entry. Complementary oscillations are seen in the  $0 \rightarrow 0$  transition probability. Finally, fig. 1 clearly shows the distinction between true resonances and the broad artificial oscillations characteristic of the non-propagative  $R$ -matrix method [4].

Experimentally, with a 500 K surface, the  $J+1$  resonances appear to desorb dissipatively, appearing on-

ly as dips in the most strongly perturbed  $0 \rightarrow J$  transition probabilities. Experiments now in progress on cryogenic Ag(111) surfaces [5] will provide better data for detailed comparison with our results. In the future we hope to obtain more quantitative agreement by including both diffractive and dissipative effects in the calculation and a more realistic potential. These calculations confirm, however, the adequacy of the bound vibration-rigid rotor estimates of the resonance energies, provided the first-order level shift is added to the BVRR energies.

## References

- [1] J.P. Cowin, C.F. Yu, S.J. Sibener and J.E. Hurst, *J. Chem. Phys.* 75 (1981) 1033.
- [2] M.W. Cole and D.R. Frankl, *Surface Sci.* 70 (1978) 585, and references therein.

- [3] R M Logan, Mol. Phys 17 (1969) 147;  
G. Wolken, Chem. Phys Letters 21 (1973) 373; J. Chem.  
Phys. 59 (1973) 1159; 62 (1974) 2730;  
F O. Goodman and W S. Liu, Surface Sci 49 (1975) 417;  
U. Garibaldi, A.C. Levi, R. Spadacini and G.E. Tommei,  
Surface Sci. 55 (1976) 40,  
R B. Gerber, A.T. Yannon, T. Shimoni and D.J. Kouri, J.  
Chem. Phys 73 (1980) 4397.
- [4] D J. Zvjac, E J. Heller and J C. Light, J. Phys. B8 (1975)  
1016;  
D J Zvjac and J.C. Light, Chem. Phys. 12 (1976) 237.
- [5] C.F. Yu, C.S. Hogg and S.J. Sibener, to be published.

### ERRATA

M.E. Kellman, Dynamic Jahn–Teller effect for degenerate states of coupled vibrations in van der Waals clusters, Chem. Phys. Letters 87 (1982) 171.

Fig. 1 should have, for trimers,  $E(I)$  at  $-1.93$  and  $E(II)$  at  $1.43$ ; for tetramers,  $F_2(I)$  at  $-1.85$  and  $F_2(II)$  at  $2.35$ . In the text, the corresponding frequencies in  $\text{cm}^{-1}$ , with erroneous values in parentheses, are:  $934.4$  ( $935.7$ ) and  $957.9$  ( $956.7$ ) for trimers;  $935.0$  ( $936.2$ ) and  $964.4$  ( $963.1$ ) for tetramers. The discussion is not affected by these revisions.

I would like to thank Dr. J. Reuss for bringing my attention to this matter.

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D.W. Davis, On atomic potential energies, proton affinities and photoemission, Chem. Phys. Letters 87 (1982) 353.

The address, "Haagen-Smith Laboratory" should read "Haagen-Smit Laboratory". Table 1,  $R_{ab}$  should read  $R_{ap}$ . Table 1, footnote c), "energy minimum for  $\Delta H$ " should read "energy minimum for  $AH$ ". Page 355, first paragraph, last sentence, " $A_n$  and  $B_n$  integrals" should read " $A_n$  integrals".