國立交通大學光電工程研究所博士

# 表面吸附雙原子分子的轉動能階及其外加電場效應的研究
# Studies on the Rotational Energy Levels and the External Electric Field Effect of Adsorbed Diatomic Molecules

石豫臺

## 中文摘要

本論文分為兩個主要部份，第一部份是研究表面吸附雙原子分子的轉動能態；第二部份是研究自由及表面吸附極性分子的外加電場效應。在第一部份中，我們利用剛性轉子模擬雙原子分子的垂直及水平吸附組態，而這轉子的空間運動受到一有限高角錐井的局限。除了極向禁制位能外，我們也一併考慮了 Kronig-Penney 型態及正弦型態的方位調制。這兩種型態的方位調制具有吸附位置的局部對稱性。我們發現將轉動能階視為禁制角度的函數並對其作圖時，會顯現出振盪行為。這種振盪行為的物理根源於共振穿透現象。我們也發現當方位調制增強時，轉動能階將聚集成帶。我們利用禁制轉動的解計算了脫附分子的轉動能態分布，並得到這些分布的非 Boltzmann 特性。這些結果相當符合先前的實驗數據。在第二部份中，我們利用變分法計算在外加電場作用下的自由及表面吸附極性分子的轉動能量。我們的結果顯示，當自由極性分子處於強電場中，其轉動能量會有很大的偏移。這個結果與先前的矩陣對角化計算結果相當吻合。在另一方面，對於表面吸附的極性分子，我們的計算結果顯示，當電場強度無法與表面禁制位能相比擬時，分子轉動能量的 Stark 偏移會受到角錐井的抑制。但是當外加電場很強時，分子的轉動能量會有很大的負偏移。此外，我們還發現非常強的電場會導致垂直吸附分子的翻轉或導致水平吸附分子的吸附組態由水平變成垂直。

關鍵字：吸附分子; 轉動能階; 外加電場; 禁制轉動; 轉動能態分布; 史塔克偏移

Abstract

This dissertation contains two main parts: the first part is devoted tothe studies on the rotational states of adsorbed diatomic molecules; and thesecond part is devoted to the studies on the external electric field effect ofthe free and adsorbed dipole molecules. In the first part,both vertical andhorizontal adsorption configurations of a diatomic molecule were modeled as the rigid rotor with which the spatial motion wasconfined by a finite conical well. In addition to the polar hinderingpotential, the Kronig-Penney and sinusoidal azimuthal modulations whichbear the local symmetry of the adsorption site were incorporated. We foundthat the rotational energy levels exhibit oscillatory behavior when plottedas functions of the hindrance angle. The physical origin of the oscillatorybehavior was ascribed to the phenomenon of the resonance transmission. Wealso found that the rotational levels were grouped into bands when theazimuthal modulation strength was increased. The solutions were used tocalculate the rotational-state distributions of desorbed molecules. Thenon-Boltzmann feature of the distributions was obtained. Our results werein agreement with previous experimental data. In the second part, the variational calculations of the rotationalenergies of both free and adsorbed dipole molecules in external electricfields were presented. Our results showed that, for the free dipolemolecules placed in strong electric fields, the rotational energies havelarge shifts. The results agreed very well with the previous diagonalizationcalculations. On the other hand, for the adsorbed dipole molecules, ourresults showed that the Stark shifts of the rotational energies weresuppressed by the conical well if the field strength is not comparable withthe hindering potential.
However, when the applied field is strong, largenegative shifts were found. Furthermore, we also showed that a very strongelectric field will induce the flipsof the vertically adsorbed moleculesor the change of adsorption configurationfrom horizontal to vertical forthe horizontally adsorbed molecules.

Key words：Adsorbed Molecules; Rotational Energy Levels; External Electric Field; Hindered Rotation; Rotational-state Distributions; Stark Shift