

Shaping surface landscapes with molecules: rotationally induced diffractive scattering of H₂ on LiF(001) under fast grazing incidence conditions

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Synopsis From six-dimensional solutions of the time-dependent Schrödinger equation, we show that diffraction of H₂ molecules by LiF(001) surfaces under fast grazing incidence conditions depends on the initial rotational state of the molecule, while rotationally inelastic processes are irrelevant. Due to the anisotropy of the impinging projectile, rotation favors high-order diffraction peaks at incidence directions with a precise symmetry. As high-order diffraction carries more detailed information on the molecule-surface interaction than available from low-order diffraction spectra, our results suggest that H₂ could be more useful than atoms for surface characterization at grazing incidence.

Following the observation in 2007 of atomic and molecular diffraction by surfaces under fast (0.2-20 keV) grazing (1-3°) incidence conditions [1, 2], the potential to characterize surface properties with more accuracy than with traditional atomic diffraction techniques was immediately realized. As in traditional low energy diffraction, most experiments of diffraction under fast grazing incidence (DFGI) have been performed by using light atomic projectiles, mainly H and He, since their internal structure is preserved upon scattering by the surface, thus simplifying the analysis of the measured spectra. Nevertheless, DFGI has also been reported by using H₂ and D₂ molecular projectiles, although the complications arising from the additional degrees of freedom (molecular rotation and vibration) and the lack of theoretical support to understand their role in this context has prevented further developments in this direction

One of the main problems in interpreting H₂ DFGI experiments is that the initial rovibrational state of the molecule is not known. Lack of knowledge on the actual projectile rovibrational distributions and the role played by vibrational and rotational excitations in DFGI is therefore the current bottleneck in the field, which prevents experimentalists from exploiting the huge potential of molecular projectiles.

In this context, help from theoretical modeling with real predictive power is crucial to guide experimental research. This modeling requires, at least, the evaluation of accurate potential en-

ergy surfaces (PES) to describe the H₂-surface interaction and the solution of the time-dependent Schrödinger equation (TDSE) that governs the scattering dynamics in which all the H₂ degrees of freedom are taken into account.

By doing so, we show that diffraction strongly depends on the initial H₂ rotational state, while it barely depends on the initial vibrational excitation. This behavior is entirely due to elastic scattering processes in which the initial rotational angular momentum of H₂ is preserved, thus greatly simplifying the analysis of the observed spectra. At specific incidence directions, the appearance of high-order diffraction peaks reveals a high degree of rotational excitation in the incident molecular beam, which must therefore be taken into account to correctly interpret experimental spectra, but provides, in the absence of inelastic processes, the ideal scenario for a detailed characterization of the surface. These conclusions are supported by the good agreement between our results and those of recent experimental measurements [3].

References

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