A novel approach to deconvolve overlapping features in molecular spectra: Monte Carlo random walk routine and its application

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Synopsis A new method, basing on Monte Carlo random walk routine, to unfold complicated features in molecular spectra has been developed, which can extract the absolute differential cross sections for the excitation states of diatomic molecules.

The accurate dynamic parameters of atoms and molecules are of critical importance to understand the underlying physical mechanism involving electron/photon excitation or ionization processes, and to test the related theoretical methods [1]. The measured spectra (photoabsorption spectra, electron energy-loss spectra, etc.) can be formulated by a spectral fitting function, which is the convolution of overlapping peaks of the vibrational sublevels from different electronic states and the instrumental response function [2-4]. In other words, these peaks can be approximately depicted by the energies and Franck-Condon factors of the vibronic levels which are modified by the instrumental response function.

A novel procedure has been established which allows for unfolding the overlapping molecular electronic state structure in many kinds of spectra. It can extract the absolute differential cross sections for excited states of diatomic molecules from the observed molecular spectra. In contrast to the least-squares fitting technique [2-5], the present program repeatedly changes the values of the parameters in the spectral fitting function by Monte Carlo random walk method in order to minimize the variance between the experimental spectrum and the represented one. This routine can highly increase the odds of the global minimum variance hunting relative to the least-squares fitting [2-5]. In addition, the relevant energies and Franck-Condon factors for the vibronic levels of the individual electronic states are collected from the published literatures as the input data to improve the reliability of the spectrum deconvolution.

Figure 1 demonstrates an example of this program to unfold the electron energy-loss spectrum of nitrogen within 8-12.2 eV by fast electron scattering at 1.5 keV, which shows that the fitting result is in good agreement with the experiment.

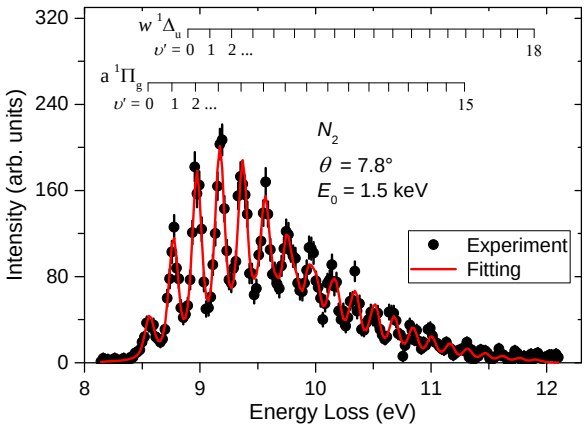

Figure 1. Typical electron energy-loss spectrum for excited states of N_2 by fast electron impact at 1.5 keV and a scattering angle of 7.8°, along with the deconvolution by Monte Carlo random walk method.

References

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