1 Atomic and Molecular Science

1-1 Shape-Resonance-Enhanced Vibrational Effects in the Angular Distributions of C 1s Photoelectrons from Fixed-in-Space CO Molecules

Measurements of photoelectron angular distributions from fixed-in-space molecules provide us with detailed information of the photoionization dynamics, since the angular distributions are determined by the dipole matrix elements and experimental geometries. Such measurements were initiated at the PF several years ago, and unveiled the photoionization dynamics of molecular shape resonances. However, all the measurements were made with vibrationally-unresolved resolution. Recently we have succeeded in measuring C 1s photoelectron angular distributions in the shape resonance region from fixed-in-space CO molecules with vibrationally-resolved resolution for the first time [1]. Figure 1 shows typical examples of our molecular-frame photoelectron angular distributions (MF-PAD). As can be seen in Fig. 1, the MF-PAD depends remarkably on the final vibrational state.

The resulting behavior can be understood as follows. Because the peak position and width of the shape resonance are sensitive functions of the internuclear distance R, the dipole matrix elements must also vary rapidly with R. Within the barrier model for shape resonances, a small change in R can affect the balance between the attractive and repulsive forces which combine to form the potential barrier. The small change in R is realized due to the fact that transitions to different final vibrational states preferentially sample different values of R. In particular, because the bond length in the final ionic state is shortened with respect to the initial state in this case, the maximum overlap between the initial and final vibrational wave functions takes place for larger values of R as the vibrational quantum number v_f of the final ionic state is increased (see Fig. 1). As a consequence, the dipole matrix elements weighted with the product of the initial and final vibrational wave functions vary with v_f, i.e., the MF-PAD varies with v_f. Indeed theoretical results which have calculated the dipole matrix elements weighted with the product of the vibrational wavefunctions reproduce the non Franck-Condon behavior of the experimental MF-PAD fairly well [1].

The resulting non Franck-Condon behavior observed here for the first time is quite general and similar phenomena must be observable in other systems. The study of this behavior will shed new light on the shape resonance dynamics of molecules.

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References
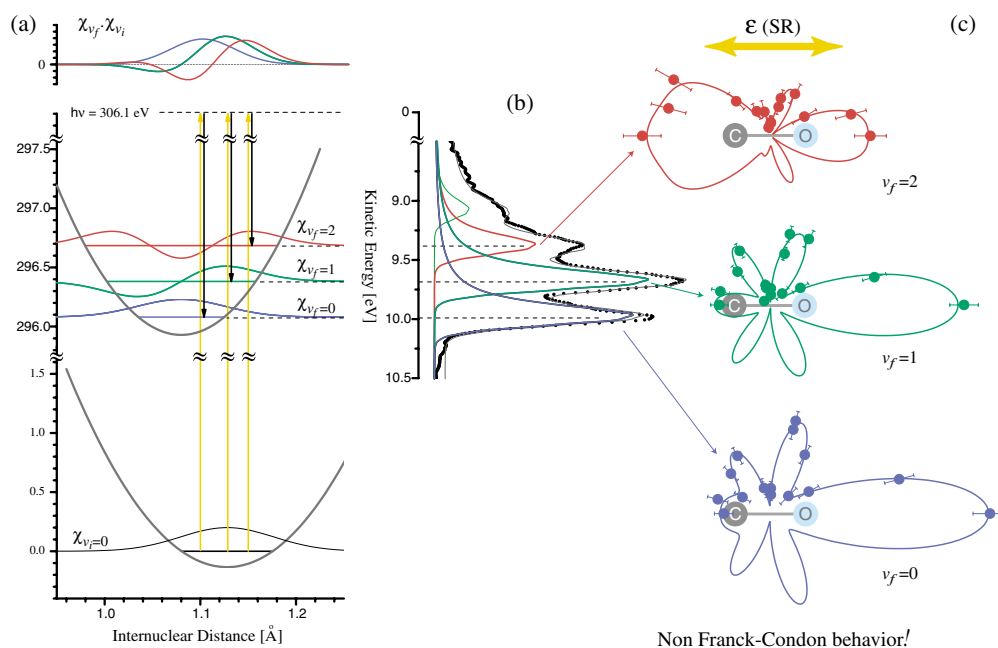
[1] J. Adachi *et al.*, *Phys. Rev. Lett.* submitted.

Figure 1
(a) Schematic potential curves of the CO molecule, the initial and final vibrational wavefunctions, and their product. (b) The vibrationally resolved C 1s photoelectron spectrum. (c) MF-PAD's for different vibrational final states at $h\nu$ = 306.1 eV. The polarization vector of the incident light is parallel to the CO molecular axis.