

Angle-resolved Auger electron spectroscopy providing a sensitive access to a hidden vibronic coupling

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Synopsis In angle-averaged spectra of molecules, vibronic coupling usually induces weak dipole-forbidden transitions by the excitation intensity borrowing mechanism. Here we present a complementary theoretical and experimental study of the resonant Auger decay of CH₄ and Ne. We demonstrate that vibronic coupling plays an important role in the formation of the angle-resolved spectra by involving the decay rate borrowing mechanism. We show that angle-resolved Auger spectroscopy can provide very insightful information on the strength of vibronic coupling in general.

Beyond the typically successful Born-Oppenheimer approximation nuclear and electronic motion is coupled by vibronic coupling [1-3]. It is a significant effect in the spectroscopy of molecules and solids. But also radiationless decays in large polyatomic (bio-)molecules are governed by this process [4,5]. A novel insight into the vibronic coupling mechanism is given here by the employment of angle-resolved Auger-electron spectroscopy which shows a dramatic effect on the angular distribution of those electrons. In a prototypical study we investigate the C *1s* → *nl* Rydberg excitation of methane and the subsequent Auger decay. In this excitation region the symmetric stretching mode is most prominent in the angle averaged excitation spectrum, but additional resonances were observed which are dipole-forbidden and only visible due to the excitation intensity borrowing mechanism [6].

When studying the angle-resolved decay spectra of those resonances new features appear which cannot be explained by this borrowing mechanism. In an ab initio theoretical investigation we find that the vibronic coupling also gives rise to a decay rate borrowing mainly visible in the angular distribution of the emitted electrons.

We will present the experimental results obtained by extensive studies at the PLEIADES beamline of the synchrotron radiation facility SOLEIL using a hemispherical angle resolving

spectrometer together with the ab initio calculations performed within the single center method in the relaxed core Hartree-Fock approximation on potential curves computed in the multireference configuration interaction method. Different models were used but dramatic differences of the calculated and experimental results still prevailed. Only when the mechanism of decay rate borrowing is introduced the results agree [7].

To cross check the electronic part of the theoretical results we performed an additional investigation on the isoelectronic Ne atom. Here the electronic part of the process is comparable to the CH₄ case and, of course, no vibronic coupling can take place.

All of the results, i.e. computational and experimental for Ne and CH₄, will be presented and discussed here and a detailed discussion and description of the theory utilized to obtain the results is available in reference [7].

References

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