

## INTRAMOLECULAR DYNAMICS OF MOLECULAR IONS

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The Fourier transform of an electronic spectrum gives a direct dynamic information on the nuclear motion of a wave packet on the potential energy surface of the final state reached in the electronic transition, at least during the first few molecular vibrations. The method is valid for both adiabatic and non-adiabatic situations. It has proved its usefulness in the study of molecular processes such as Duschinsky effect, fast predissociations and internal conversions.

## INTRODUCTION

There exists a general method in quantum mechanics which provides a way to extract dynamic information from an absorption or emission spectrum. The method elaborates on the well-known rule derived from the Heisenberg uncertainty principle according to which an increase in the band width indicates that the state under study is engaged in a dynamic process. A more detailed formulation asserts<sup>1)</sup> that the Fourier transform of a spectroscopic profile gives rise to a so-called autocorrelation function which measures the persistence in time of some physical quantity. The nature of this quantity depends on the energy domain in which the optical spectrum is determined. The method has previously been applied to IR, Raman, NMR and other branches of spectroscopy<sup>2)</sup> and has considerably increased our knowledge on intermolecular forces. Recent research by Heller<sup>3)</sup> has shown that the correlation function associated with an electronic spectrum gives information about the way a wave packet propagates on the potential energy surface of the final electronic state involved in the transition. More precisely, the correlation function is equal to the modulus of the overlap integral between the initial position of the wave packet and its instantaneous position at a later time :

$$C(t) = |\langle \phi | \phi(t) \rangle| = \int_{-\infty}^{+\infty} \frac{I(E)}{E} e^{-iEt/\hbar} dE \quad (1)$$

where  $C(t)$  is the correlation function.  $|\phi\rangle$  and  $|\phi(t)\rangle$  represent respectively the nuclear wave packet at the initial time and at some later time  $t$  as it propagates on the potential energy surface of the electronic state under study, the Dirac bracket represents integration over the nuclear co-ordinates, and  $I(E)$  represents the intensity of the absorption band as a function of the energy  $E$ .

In practice, the Fourier transform of an experimental spectrum has to be corrected<sup>4)</sup> for finite energy resolution if dependable information is to be obtained, and for rotational and spin-orbit coupling widths if the vibrational motion only is of interest. The resulting vibrational correlation function then gives rise to a reliable description up to a time of about

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$10^{-13}$  s. In other words, the behaviour of the molecule can be studied during its first few molecular vibrations. It can also be demonstrated<sup>5)</sup> that the validity of the method is not limited to purely adiabatic processes, i.e., to processes in which a single electronic state is involved. It is also valid when predissociations and radiationless transitions between two electronic states take place as a result of either spin-orbit coupling or breakdown of the Born-Oppenheimer approximation.

We shall now give a brief account of the application of this method to the intramolecular dynamics of ionized molecules. In this particular case, the energy spectrum to be used is a photo-electron spectrum. Only a brief discussion is given, and reference is made to papers where a full account can be found.

#### ADIABATIC PROCESSES

The analysis of experimental results confirms that a wave packet remains Gaussian if it moves in a harmonic potential<sup>6)</sup>. This has been observed<sup>4)</sup> for states  $X^2\Sigma_g^+$  and  $B^2\Sigma_u^+$  of  $N_2^+$ . However, the wave packet breaks up into two or possibly several smaller parts if it moves in an anharmonic force field. This takes place<sup>4)</sup> in state  $A^2\Pi$  of  $N_2^+$ .

Nuclear motion on multidimensional surfaces is of course more complex. If the Duschinsky effect<sup>7)</sup> is negligible, i.e., if the normal coordinates of the lower state remain appropriate for the description of the upper state, then the multidimensional motion can be split into a superposition of one-dimensional harmonic oscillations. This means, in classical terms that the centre of the wave packet executes a Lissajous motion in configuration space. The Duschinsky rotation is shown<sup>8)</sup> to be small in the case of state  $\tilde{X}^2B_1$  of  $H_2O^+$ , larger, but still relatively unimportant for state  $\tilde{X}^2B_{3u}$  of  $C_2H_4^+$ , and extremely important<sup>4)</sup> in the case of state  $\tilde{B}^2\Sigma^+$  of  $HCN^+$ . In addition to the Duschinsky effect, which is limited to an interaction among normal modes belonging to the same symmetry species, one also has to consider the energy flow from optically active modes (which necessarily belong to the totally symmetrical representation) to optically inactive acceptor modes which possess some antisymmetrical character. The energy flow is irreversible because a linear combination of the acceptor modes will give rise to the reaction coordinate. This energy redistribution is found to be slow with respect to the time scale of the experiment, at least in the case<sup>8)</sup> of states  $\tilde{X}^2B_1$  of  $H_2O^+$  and  $\tilde{X}^2B_{3u}$  of  $C_2H_4^+$ .

#### NON-ADIABATIC PROCESSES

The very fast processes frequently encountered in photochemistry, ion chemistry and high-energy chemistry frequently result from strong non-adiabatic coupling between potential energy surfaces. We have studied a predissociation problem in a dynamic way. It is observed<sup>5)</sup> that the four lowest vibrational levels of  $HBr^+ A^2\Sigma^+$  are not predissociated, whereas the upper ones are strongly coupled with the dissociation continuum of a  $^4\Pi$  repulsive state. The lifetime of the latter is of the order of one-half vibrational period. The correlation function shows clearly<sup>5)</sup> that the wave packet travels from the Franck-Condon zone to the crossing point in a time equal to one-half vibrational period. There, it splits into two parts. One part switches from the original  $^2\Sigma^+$  state to the repulsive quartet state and travels away to infinity along the repulsive curve, whereas the second part remains trapped in the bound potential.

For a polyatomic molecule, ab initio calculations often reveal the presence of conical intersections between two potential energy surfaces. This brings about a very strong non-adiabatic interaction and leads to extremely fast relaxation processes. Such an interaction takes place between states  $\tilde{B}^2B_2$  and  $\tilde{A}^2A_1$  of  $H_2O^+$ <sup>9)</sup> and between states  $\tilde{A}^2B_{3g}$  and  $\tilde{X}^2B_{3u}$  of  $C_2H_4$ <sup>10)</sup>.

Therefore, the energy spectrum of states  $\tilde{B}$  of  $H_2O^+$  and  $\tilde{A}$  of  $C_2H_4^+$  consists in both cases of a broad and irregular structure. The corresponding correlation functions decrease rapidly

with time and reflect the steps along which the relaxation proceeds. The decay law cannot be fitted to a conventional rate expression.

#### CONCLUSIONS

In summary, the study of a correlation function allows a direct visualization of wave packet motion during the first few vibrational periods. It enables one to study ultrafast internal conversions, and gives a dynamic interpretation of broad and diffuse spectra which could not be accounted for in terms of conventional models.

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