

COUPLINGS BETWEEN NORMAL MODES STUDIED BY THE CORRELATION FUNCTION. DUSCHINSKY EFFECT AND FERMI RESONANCE

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The dynamical information contained in a correlation function obtained by the Fourier transform of an electronic spectrum can be used to study strong intermode couplings, such as the Duschinsky effect (DE) and the Fermi resonance (FR). Both of them complicate the calculation of the correlation function by destroying its factorizability. In some particular cases, the DE can greatly simplify the form of the correlation function by concealing one of its inherent frequencies. The DE never leads to a beat or to a systematic decrease of the correlation function. A simple classical approximation for the correlation function which takes into account the Lissajous motion of the center of the wave packet, but does not allow for its deformation or spreading is found to be useful in a harmonic model. The FR leads to a beat in the correlation function which results from a periodic energy transfer from the active to the inactive mode. A practical method is given to extract the perturbed and unperturbed energies as well as the coupling matrix element of a FR from a low-resolution spectrum by Fourier transformation of just that part of the spectrum which corresponds to the quasidegenerate interacting states. The case of the $\bar{B}^2\Sigma_u^+$ state of CS_2^+ is treated as an example.

1. Introduction

The information which can be obtained from the study of an optical transition is not limited to energetic and structural, i.e. to static aspects. Every dipolar spectrum contains dynamical information expressed in terms of a correlation function which is given by the Fourier transform of the optical profile. In the case of electronic spectra, the correlation function provides information on the time evolution of a wave packet on the potential energy surface of the upper electronic state involved in an electronic transition [1-12]. In the Condon approximation, the optical transition propels the vibrationless nuclear wavefunction Φ of the lower electronic state on the potential energy surface of the upper electronic state. $\Phi(t)$ is then no longer a stationary wavefunction, but a wave packet which propagates on the upper surface. The Fourier transform of an electronic band is equal to the time dependent overlap integral $\langle \Phi | \Phi(t) \rangle$

$$\langle \Phi | \Phi(t) \rangle = \frac{\int dE I(E) \exp(-iEt/\hbar)/E}{\int dE I(E)/E} \quad (1.1)$$

and the correlation function, denoted $C(t)$, is defined to be the modulus of this quantity:

$$C(t) = |\langle \Phi | \Phi(t) \rangle|. \quad (1.2)$$

Eq. (1.1), which has been derived by Heller [1], forms the basis of the correlation function method. It establishes a link between spectroscopy and molecular dynamics and has been applied to a large number of physicochemical problems [2-12].

We have chosen to apply the method to the study of dynamical processes in ionized molecules. In this case the initial information is a photoelectron spectrum. Practical problems peculiar to this method concerning data handling, have been discussed in refs. [5-9]. Approximate procedures have been developed to correct the original spectrum for finite energy resolution, Doppler and rotational widths, and spin-orbit coupling.

In practice, however, these corrections become unreliable at times longer than 10^{-13} s (2×10^{-13} s at most in favourable cases). Thus, the method provides information on the fate of a molecular ion dur-

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ing the first few vibrational motions which immediately follow its creation. Hence, only ultrafast processes brought about by very strong perturbations can be studied by this technique. Non-adiabatic transitions induced by a conical intersection and even by strong spin-orbit coupling have already been studied both experimentally [6–8] and theoretically [6,10,11] by this method. Weak perturbations such as Coriolis coupling are not expected to lead to detectable effects.

The present paper concentrates on two strong nuclear perturbations, i.e. the Duschinsky effect (DE) and the Fermi resonance (FR). The questions which we wish to address are: How do these perturbations affect a correlation function? What information about the intermode couplings can be obtained from the correlation function? Are they more easily detected by this method than in an optical spectrum?

At this point, we wish to emphasize that our interest is not in the development of theoretical procedures to calculate a correlation function. Such methods can be found in numerous papers written by Heller and co-workers [1–4], Köppel [10], Deharang [11,13], Brickmann [14], and others [9,12]. Instead, we wish to provide the experimentalist with a few guidelines to help him to interpret qualitatively a correlation function and to extract as much dynamical information as possible. The paper is organized as follows. The useful zero-order approximation which consists in representing a correlation function of a polyatomic molecule by a product of independent diatomic-like functions is quickly reviewed in section 2. Then, in sections 3 and 4, we discuss two different types of intermode couplings, DE and FR, which destroy this factorizability.

2. Factorization of the vibrational correlation function

In a polyatomic molecule, the correlation function describes a nuclear motion which, in general, involves several degrees of freedom simultaneously. It is important to understand under what conditions this function can be factorized into a product of one-dimensional functions describing the motion along one normal coordinate only.

The normal coordinates of two electronic states in a polyatomic molecule are in general related by

$$q_j^{\text{II}} = \sum_{k=1}^M a_{jk} q_k^{\text{I}} + b_j, \quad j=1, \dots, M, \quad (2.1)$$

where the quantities b_j are the differences in the equilibrium positions of the two electronic states. The matrix a_{jk} accounts for the rotation and scaling of the normal coordinates, and M is equal to the number of vibrational degrees of freedom. If the electronic states in question are bound, then, by introducing mass-weighted normal coordinates, one obtains an orthogonal matrix a_{jk} [15]. If the electronic transition leads to dissociation, it is necessary to consider a more general affine a_{jk} matrix [16,17].

Sufficient conditions of factorizability of the correlation function can be formulated as follows.

(1) The lowest vibrational wavefunction of the first electronic state must have the form

$$|\Phi\rangle = \prod_{j=1}^M |j\rangle, \quad (2.2)$$

where the wave function $|j\rangle$ depends only on the normal coordinate q_j^{I} .

(2) The nuclear Hamiltonian of the upper electronic state should be separable into the normal coordinates of this state

$$H^{\text{II}} = \sum_{k=1}^M H_k(q_k^{\text{II}}), \quad (2.3)$$

i.e. the intermode coupling due to anharmonicity should be unimportant.

(3) The a_{jk} matrix in (2.1) should be diagonal, i.e. the DE should be negligible. In this case the normal coordinates of the two states are related by

$$q_j^{\text{II}} = \lambda_j q_j^{\text{I}} + b_j, \quad j=1, \dots, M. \quad (2.4)$$

If all of these assumptions are valid, we can write the expression for the correlation function in the form

$$\begin{aligned} C(t) &= \prod_{j=1}^M |\langle j | \exp(-iH_j^{\text{II}} t/\hbar) | j \rangle| \\ &= \prod_{j=1}^M |\langle j | j(t) \rangle| = \prod_{j=1}^M C_j(t). \end{aligned} \quad (2.5)$$

The present paper discusses two types of intermode mixing which prevent the factorization of the correlation function. The first one is the DE for active modes, which leads to the breakdown of assumption (3). The second type of intermode mixing is that

leading to the breakdown of assumption (2), the FR between active and passive modes being the most common example.

3. Duschinsky effect

To study the influence of the DE on the correlation function we investigate a simple two-dimensional model. The initial electronic state is characterized by the normal coordinates $\{X, Y\}$, and the final one by the set $\{x, y\}$. The potential surfaces of both states are supposed to be harmonic. Thus, the vibrational Hamiltonian for the initial electronic state in mass-weighted coordinates has the form

$$H^I = 0.5(-\hbar^2 \partial^2 / \partial X^2 - \hbar^2 \partial^2 / \partial Y^2 + \omega_X^2 X^2 + \omega_Y^2 Y^2). \quad (3.1)$$

The vibrational Hamiltonian for the final electronic state is obtained by replacing $\{X, Y\}$ by $\{x, y\}$ in eq. (3.1). This simple model can be used to describe, e.g., the electronic and photoelectron spectra of symmetric bent triatomic molecules when the excitation of the final electronic state is not too high and when there is no substantial energy transfer via FR to the antisymmetric normal mode.

Before time $t=0$, our system is described by the lowest vibrational wavefunction of the initial electronic state,

$$\Phi = (ab/\pi^2)^{1/4} \exp[-0.5(aX^2 + bY^2)], \quad (3.2)$$

with $a = \omega_X/\hbar$, $b = \omega_Y/\hbar$. At $t=0$, it makes a Franck-Condon transition to the final electronic state. To describe the evolution of the wave packet $\Phi(t)$ on the potential energy surface of the second electronic state, we expand Φ in the basis of the vibrational wavefunctions of the latter electronic state,

$$\Phi = \sum_{kj} c_{kj} \chi_k(x) \phi_j(y). \quad (3.3)$$

To do this, it is necessary to know the relation between normal coordinates in the two electronic states. In our case this relation can always be written

$$\begin{aligned} x &= X \cos \theta - Y \sin \theta + \alpha, \\ y &= X \sin \theta + Y \cos \theta + \beta. \end{aligned} \quad (3.4)$$

This relationship is represented in fig. 1. Using (3.4) we can rewrite (3.2) in the form

$$\Phi = (ab/\pi^2)^{1/4} \exp[-0.5p(x-q)^2 - s], \quad (3.5)$$

where

$$p = a \cos^2 \theta + b \sin^2 \theta, \quad (3.6a)$$

$$q = \alpha + (1/2p)(b-a)(y-\beta) \sin 2\theta, \quad (3.6b)$$

$$s = (ab/2p)(y-\beta)^2. \quad (3.6c)$$

The coefficients c_{kj} in (3.3) are given by

$$\begin{aligned} c_{kj} &= \iint dx dy \Phi(x, y) \chi_k^*(x) \phi_j^*(y) \\ &= (ab\hbar/p\pi)^{1/4} \int dy \phi_j^*(y) \exp[-s(y)] \\ &\quad \times \int dx \chi_k^*(x) (p/\pi\hbar)^{1/4} \\ &\quad \times \exp[-0.5p(x-q)^2]. \end{aligned} \quad (3.7)$$

The integrals over x were evaluated using available analytical formulae [18]. After this, the integrals over y were calculated numerically using a simple trapezoidal rule. Given the c_{kj} 's, we can immediately write the expression for the correlation function,

$$\begin{aligned} C(t) &= \left(\sum_{kj} |c_{kj}|^4 \right. \\ &\quad \left. + \sum_{kj \neq nm} |c_{kj}|^2 |c_{nm}|^2 \cos(\omega_{kj, nm} t) \right)^{1/2}. \end{aligned} \quad (3.8)$$

Here, $\omega_{kj, nm} = (E_{kj} - E_{nm})/\hbar$, where the vibrational energies, E_{kj} , of H^{II} are given by

$$E_{kj} = \hbar\omega_x(k+0.5) + \hbar\omega_y(j+0.5). \quad (3.9)$$

In order to illustrate the influence of the DE on the

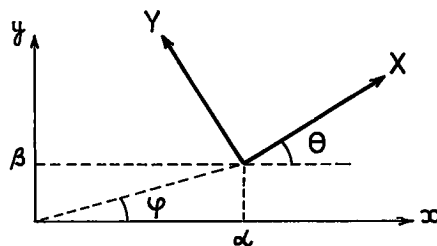


Fig. 1. Mutual location of the coordinate systems of the two electronic states for a Duschinsky effect: X, Y are the coordinates of the initial state; x, y , those of the final state.

correlation function we calculated the latter for two electronic states with $\omega_x=1600\text{ cm}^{-1}$, $\omega_y=3800\text{ cm}^{-1}$, and $\omega_x=1400\text{ cm}^{-1}$, $\omega_y=3200\text{ cm}^{-1}$. The values of the frequencies were chosen to simulate the potential energy surfaces of the ground electronic state of H_2O and the $\tilde{X}^2\text{B}_1$ electronic state of H_2O^+ . However, since the DE is estimated [19] to be small in this case, some additional flexibility was introduced into the model. The correlation functions were calculated for different values of the parameters φ and θ describing the mutual location of the two electronic states. The parameter $\rho=(\alpha^2+\beta^2)^{1/2}$ was taken to be equal to 0.1 \AA . Such a value of ρ allowed us to obtain substantial variations in the correlation function for different values of θ and φ , while keeping the number of significantly excited levels of the second electronic state reasonably small. In practice some 20 to 40 terms were included in expansion (3.3).

One important point concerning the concept of DE should be mentioned here. The mutual location of two normal coordinate reference frames is described by two groups of angular parameters (fig. 1). The first group contains all the angles defining the direction of the vector connecting the centers of the two coordinate systems (angle φ in our case), whereas the second contains all the angles fixing the mutual orientation of the axes of the two systems (angle θ in our case). There is a significant difference between these two groups of parameters for the following reason. The parameters of the first group can be changed without changing the parameters of the second group. This is true in both reference frames. On the other hand, this is not always the case for the second group of parameters.

Usually, the DE is defined as arising from non-zero values of the second group of parameters only. This definition is appropriate when one studies the DE for a fixed mutual position of the two systems of normal coordinates. The situation is more complicated when one is interested in the global features of the DE, i.e. its dependence on angular parameters. In this case, the physical content of the concept of a DE depends upon which of the two coordinate systems is chosen as a reference frame. For example, in a two-mode case (fig. 1), if one works in the coordinate system of the second electronic state, the DE is described by the change of the angle θ for constant values of ρ and φ . But, from the point of view of the initial electronic

state, this procedure results not only in a rotation of the second system of coordinates but also in the displacement of its center along a circle of radius ρ . Thus, we see that for investigating the global features of the DE, both groups of molecular parameters are important.

The first question which arises within the framework of the correlation function method is to what extent a knowledge of the correlation function alone allows one to determine the parameters, θ and φ . The answer to this question can be easily obtained from eqs. (3.5)–(3.8). In table 1, we list all 6 invariant pairs $\{\theta_i, \varphi_i\}$ and their corresponding values $\alpha_i, \beta_i, q_i(y), s_i(y)$, which give the same correlation function.

The existence of the most part of these invariant pairs is caused by the symmetry properties of the harmonic approximation. It follows that in real cases, when the anharmonicity effects are small, it will be very difficult (if possible at all) to obtain a unique set of parameters θ and φ from the correlation function only.

We shall study the DE from the point of view of the final electronic state. This will help us to clarify the physics underlying this effect. On the basis of the results of numerous calculations, out of which we present only those given in figs. 2 and 3, we can characterize the deformation of the correlation function due to the DE as follows:

- (a) A significant change in the values of both the angles θ and φ can change the qualitative aspects of the correlation function.
- (b) The correlation function is not very sensitive to the exact values of θ and φ . Small variations result in small and irregular changes in the relative heights and positions of the peaks.
- (c) Under no circumstances can the DE lead to a systematic decrease or to a beat in the correlation function.
- (d) For particular values of the angle φ ($\varphi=0$ or $\pi/2$), the correlation function of a two-dimensional model resembles qualitatively that of a one-dimensional system, whatever the value of θ (see fig. 2). A single frequency then appears in the correlation function, e.g. $\omega_x=1400\text{ cm}^{-1}$ for the cases shown in fig. 2. The corresponding effect is known in the theory of the vibrational spectra as the frequency scrambling suppression [17].

In order to gain some additional insight in the de-

Table 1
The invariant pairs $\{\theta_i, \varphi_i\}$ and their corresponding values $\alpha_i, \beta_i, q_i(y), s_i(y)$ from (3.6)

Case	θ_i	φ_i	α_i	β_i	$q_i(y)$	$s_i(y)$
1	θ	φ	α	β	$q(y)$	$s(y)$
2	$\pi+\theta$	φ	α	β	$q(y)$	$s(y)$
3	$-\theta$	$\pi-\varphi$	$-\alpha$	β	$-q(y)$	$s(y)$
4	$\pi-\theta$	$\pi-\varphi$	$-\alpha$	β	$-q(y)$	$s(y)$
5	θ	$\pi+\varphi$	$-\alpha$	$-\beta$	$-q(-y)$	$s(-y)$
6	$\pi+\theta$	$\pi+\varphi$	$-\alpha$	$-\beta$	$-q(-y)$	$s(-y)$
7	$-\theta$	$-\varphi$	α	$-\beta$	$q(-y)$	$s(-y)$
8	$\pi-\theta$	$-\varphi$	α	$-\beta$	$q(-y)$	$s(-y)$

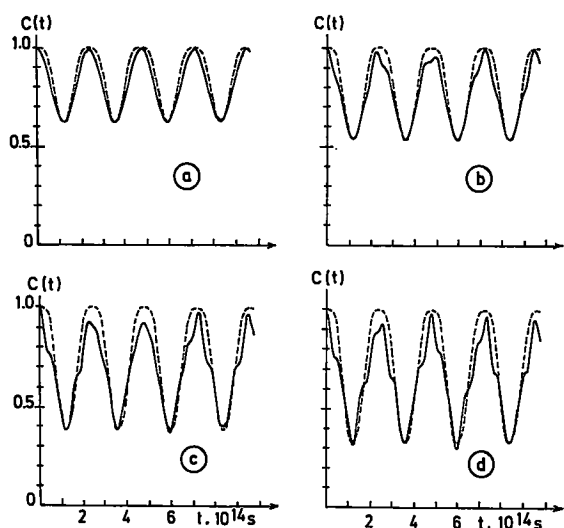


Fig. 2. Correlation function for a Duschinsky effect characterized by an angle $\varphi=0^\circ$. Solid line: converged calculations with expansion (3.1). Dashed line: classical approximation (3.12). Case (a): $\theta=0^\circ$; case (b): $\theta=30^\circ$; case (c): $\theta=60^\circ$; case (d): $\theta=90^\circ$.

pendence of the correlation function on θ and φ , we have introduced a classical approximation for the correlation function. The validity of such an approximation for describing the wave packet dynamics on the multidimensional surfaces has been discussed earlier [4,14,20–22]. As a first step we solved the Ehrenfest equations with obvious initial conditions

$$\begin{aligned} \langle x(0) \rangle &= \alpha, \quad \langle y(0) \rangle = \beta; \\ \langle p_x(0) \rangle &= \langle p_y(0) \rangle = 0 \end{aligned} \quad (3.10)$$

to obtain the trajectory of the center of the wave packet on the potential energy surface of the final

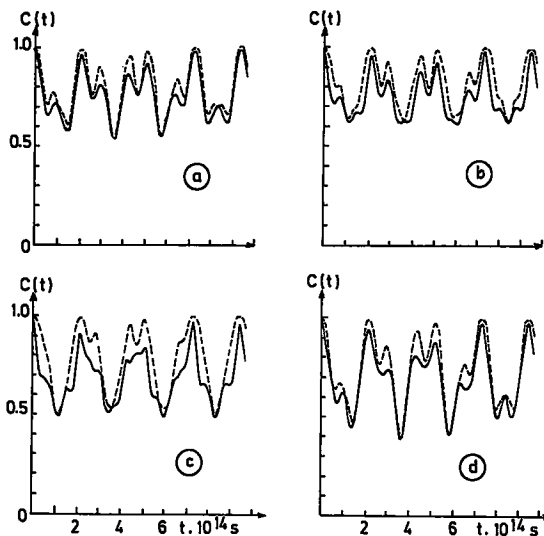


Fig. 3. Correlation function for a Duschinsky effect characterized by an angle $\varphi=30^\circ$. Solid line: converged calculations with expansion (3.1). Dashed line: classical approximation (3.12). Case (a): $\theta=0^\circ$; case (b): $\theta=30^\circ$; case (c): $\theta=60^\circ$; case (d): $\theta=-30^\circ$.

electronic state. This trajectory is described by the equations

$$\begin{aligned} \langle x(t) \rangle &= \alpha \cos \omega_x t, \\ \langle y(t) \rangle &= \beta \cos \omega_y t. \end{aligned} \quad (3.11)$$

To proceed further we assumed that the wave packet remains undeformed during its motion. This should be an acceptable first approximation in the present case of a harmonic model. We define a classical correlation function at moment t , denoted $C_{cl}(t)$, as the overlap integral between the initially created Gaussian wave packet centered at the point (α, β) and the

same wave packet centered at the point $(\langle x(t) \rangle, \langle y(t) \rangle)$. This gives us the following simple expression for $C_{cl}(t)$:

$$C_{cl}(t) = \exp\{-0.25[aX^2(t) + bY^2(t)]\}, \quad (3.12)$$

where $X(t)$ and $Y(t)$ are the coordinates of the center of the wave packet in the coordinate system of the initial electronic state. The classical correlation functions are shown in figs. 2 and 3 by dashed lines.

First of all we notice that, in spite of the severe simplifications made, the classical correlation functions reproduce surprisingly well the main features of the exact correlation functions: the positions and relative heights of the peaks, and sometimes even the fine structure of the latter. The classical correlation functions possess the same symmetry with respect to changes of θ and φ as the exact ones. Moreover the symmetry properties of the DE can be studied much more easily from (3.12) than from (3.5)–(3.8).

At the classical level of approximation, the DE can be split into two independent effects, to which we shall refer as the dynamical and the geometrical DEs. The dynamical DE is due to the change of the trajectory of the center of the wave packet. It is characterized by the corresponding Lissajous figure and depends only on the angle φ . On the other hand, the geometrical DE is due to the change of the mutual orientation of the two potential surfaces and depends only on angle θ . This effect does not change the Lissajous figure describing the motion. This separability of the DE into two independent effects takes place only if one adopts the referential of the final electronic state. From the point of view of the initial electronic state, the dynamical and geometrical DEs are mixed. In this case, changing θ not only changes the mutual orientation of the two coordinate systems, but also changes the corresponding Lissajous figure.

The frequency scrambling suppression effect [17] is now readily understood. From the classical viewpoint, such an effect occurs every time when the initial position of the center of the wave packet (α, β) coincides with one of the axes of the second electronic state referential. In this case the corresponding Lissajous figure reduces to a straight line, as for the one-dimensional case. But there are still some important differences with respect to the latter at both classical and quantal levels. Although the classical correlation function in this case is strictly periodical with

a period determined by one of the frequencies it does not behave as a cosine curve as for a really one-dimensional motion [9,22]. On the other hand, from the quantum point of view, the equality $\langle x(t) \rangle = 0$ does not prevent quantum pulsations ("breathing") of the wave packet along the coordinate x [14,20–22]. Such pulsations also deform the simple cosine form of the correlation function.

4. Fermi resonance

In this section, we study how the correlation function is perturbed by the second type of intermode mixing, taking the usual FR as an example. Heller et al. [3] have examined the systematic trends which appear when the FR involves wavefunctions of increasing energy for a given potential energy surface. A very detailed study of the energy flow brought about by a FR between two low-frequency ring torsional modes of the ground state of benzophenone has been recently carried out by Frederick et al. [23]. We present here another example where all the parameters which characterize a FR can be easily extracted from the correlation function, although this information is hidden in the photoelectron spectrum because of poor energy resolution.

Let us consider the following simplified model for a FR. Three zero-order states $|0\rangle$, $|1\rangle$ and $|2\rangle$ diagonalize the harmonic part, H_{harm} , of the nuclear Hamiltonian H of the upper electronic state,

$$H_{\text{harm}} |i\rangle = H_{ii} |i\rangle. \quad (4.1)$$

States $|1\rangle$ and $|2\rangle$, which are nearly degenerate, are coupled by anharmonic terms:

$$H_{12} = \langle 1 | H | 2 \rangle, \quad (4.2)$$

state $|0\rangle$ remaining uncoupled.

As a result of a very short light pulse, the vibrationless wavefunction of the lower electronic state Φ is propelled towards the potential energy surface of the upper electronic state. On the latter surface, it becomes a wave packet $\Phi(t)$ which can be expanded either in the basis of the eigenfunctions, $\{\psi_i\}$, of H (eq. (4.3)), or in the zero-order basis set, $\{|i\rangle\}$ (eq. (4.7)),

$$\begin{aligned}
|\Phi(t)\rangle &= a_0 |\psi_0\rangle \\
&+ a_1 \exp(-iEt/\hbar) \exp(i\Delta Et/2\hbar) |\psi_1\rangle \\
&+ a_2 \exp(-iEt/\hbar) \exp(-i\Delta Et/2\hbar) |\psi_2\rangle, \quad (4.3)
\end{aligned}$$

with $a_i = \langle \psi_i | \Phi \rangle$. The energies, E_i , of the eigenstates ψ_i are $E_0=0$, $E_1=E-\frac{1}{2}\Delta E$, $E_2=E+\frac{1}{2}\Delta E$, with E and ΔE given by

$$E = \frac{1}{2}(H_{11} + H_{22}), \quad (4.4a)$$

$$\Delta E = [(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2}. \quad (4.4b)$$

The basis set $\{\psi_i\}$ is related to the set $\{|i\rangle\}$ by an orthogonal transformation parameterized by an angle γ , ψ_0 being equal to $|0\rangle$,

$$\begin{aligned}
|\psi_1\rangle &= |1\rangle \cos \gamma + |2\rangle \sin \gamma, \\
|\psi_2\rangle &= -|1\rangle \sin \gamma + |2\rangle \cos \gamma, \quad (4.5)
\end{aligned}$$

with

$$\tan \gamma = 2H_{12}/(H_{22} - H_{11}). \quad (4.6)$$

Then:

$$\begin{aligned}
|\Phi(t)\rangle &= a_0 |0\rangle \\
&+ \exp(-iEt/\hbar) [a_1 \exp(i\Delta Et/2\hbar) \cos \gamma \\
&- a_2 \exp(-i\Delta Et/2\hbar) \sin \gamma] |1\rangle \\
&+ \exp(-iEt/\hbar) [a_1 \exp(i\Delta Et/2\hbar) \sin \gamma \\
&+ a_2 \exp(-i\Delta Et/2\hbar) \cos \gamma] |2\rangle. \quad (4.7)
\end{aligned}$$

Let us assume that state $|2\rangle$ does not carry any oscillator strength. Then:

$$|\Phi(0)\rangle = a_0 |0\rangle + (a_1 \cos \gamma - a_2 \sin \gamma) |1\rangle \quad (4.8)$$

and

$$a_1 \sin \gamma + a_2 \cos \gamma = 0. \quad (4.9)$$

Then, the correlation function reads

$$\begin{aligned}
C(t) &= [T_0^2 + T_1^2 + 2T_0 T_1 \cos(Et/\hbar) \cos(\Delta Et/2\hbar) \\
&- T_1^2 \sin^2 2\gamma \sin(\Delta Et/2\hbar) \\
&+ 2T_0 T_1 \cos 2\gamma \sin(Et/\hbar) \sin(\Delta Et/2\hbar)]^{1/2}, \quad (4.10)
\end{aligned}$$

where $T_i = |\langle i | g \rangle|^2$ are the zero-order Franck-Condon factors.

Eq. (4.10) shows that two frequencies appear in the correlation function. The higher frequency (E/\hbar)

gives rise to well-established oscillations in the correlation function. The amplitude of this oscillation is modulated by a lower frequency $\Delta E/2\hbar$. This phenomenon can be interpreted as arising from the periodic energy transfer from the active to the inactive mode and vice versa.

Such a situation is illustrated in fig. 4 for the case of the $\tilde{B}^2\Sigma_u^+$ state of CS_2^+ . The correlation function has been determined from a spectrum published in ref. [24]. Since the equilibrium geometries of the CS_2^+ $\tilde{X}^1\Sigma_g^+$ and of the CS_2^+ $\tilde{B}^2\Sigma_u^+$ states are similar, only the (000) and (100) zero-order states of CS_2^+ are populated. A FR exists, however, between (100) and (020). This resonance leads to a decrease with time of the amplitude of the high-frequency oscillation, characterized by a frequency of 650 cm^{-1} . Since the coupling is relatively weak, and allows one to see only the very beginning of the further increase of this vibration, it is hard to determine the magnitude of ΔE directly from the correlation function.

Much more insight into the FR is gained by considering the probability $P_i(t)$ for the system to be in a given zero-order state $|i\rangle$ at time t ,

$$P_i(t) = |\langle i | \Phi(t) \rangle|^2. \quad (4.11)$$

Straightforward algebra leads to the following expressions:

$$P_0(t) = T_0,$$

$$\begin{aligned}
P_1(t) &= T_1 [\cos^2(\Delta Et/2\hbar) \\
&+ \cos^2 2\gamma \sin^2(\Delta Et/2\hbar)], \quad (4.12)
\end{aligned}$$

$$P_2(t) = T_1 \sin^2 2\gamma \sin^2(\Delta Et/2\hbar). \quad (4.13)$$

To derive the values of the parameters of the FR, it is more convenient to calculate the Fourier trans-

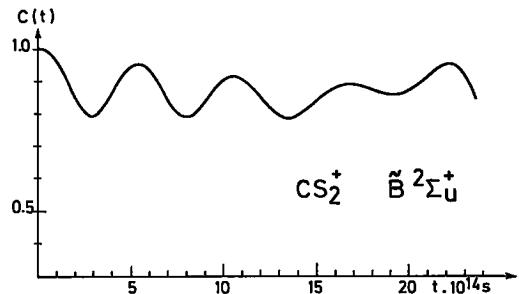


Fig. 4. Experimental correlation function of the $\tilde{B}^2\Sigma_u^+$ state of CS_2^+ .

form $F(t)$ of only that part of the spectrum that corresponds to the quasidegenerate states $|1\rangle$ and $|2\rangle$. It can be shown that

$$\begin{aligned} |F(t)/F(0)| &= [\cos^2(\Delta Et/2\hbar) + \cos^2 2\gamma \sin^2(\Delta Et/2\hbar)]^{1/2} \\ &= [P_1(t)/T_1]^{1/2}. \end{aligned} \quad (4.14)$$

This quantity goes through a minimum equal to $|\cos \gamma|$ for $t = \pi\hbar/\Delta E$.

The modulus of the Fourier transform of the $\tilde{B}^2\Sigma_u^+(100)-(020)$ part of the CS_2 photoelectron spectrum is displayed in fig. 5. One observes indeed a minimum for $t = 1.4 \times 10^{-13}$ s. This value represents the period of the energy transfer between the zero-order states. The minimum value of $|F(t)/F(0)|$ is equal to 0.496. This gives rise to $\gamma = 30.1^\circ$ and $\Delta E = 121 \text{ cm}^{-1}$. From (4.4) and (4.6), one deduces the following zero-order values:

$$H_{22} - H_{11} = 60 \text{ cm}^{-1}, \quad H_{12} = 52.5 \text{ cm}^{-1}.$$

As E was found to be equal to 650 cm^{-1} , one finally obtains the following values for the energies and zero-order frequencies:

$$\begin{aligned} \nu_1 = H_{11} &= 620 \text{ cm}^{-1}, \quad \nu_2 = \frac{1}{2}H_{22} = 340 \text{ cm}^{-1}, \\ E_1 &= 590 \text{ cm}^{-1}, \quad E_2 = 711 \text{ cm}^{-1}. \end{aligned}$$

Thus, the correlation function provides a much clearer picture of the Fermi resonance process and allows an experimentalist to derive more easily both the unperturbed and the perturbed energies as well as the coupling element. Such information, although present in the photoelectron spectrum, can only be

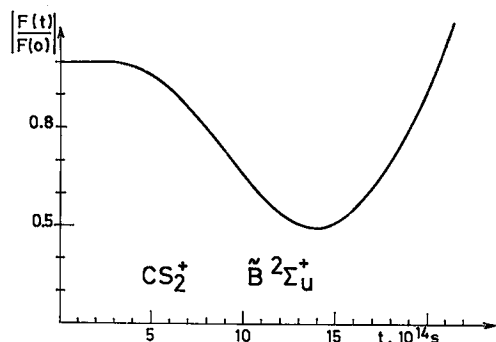


Fig. 5. Fourier transform of the (100)-(020) part of the photoelectron spectrum of the $\tilde{B}^2\Sigma_u^+$ state of CS_2^+ (eq. (4.14)).

derived with a low accuracy from that spectrum even after a deconvolution procedure [24].

5. Conclusions

Within the model considered, the DE can be viewed as a combination of two independent effects: kinematic and geometrical. This leads to a very simple explanation of the frequency scrambling suppression effect. The classical approximation is sufficient to account for the gross features of the correlation function and to study the main perturbations brought about by the DE. The latter can significantly change the form of the correlation function with respect to a simple factorized expression. In particular, it can suppress one of its inherent frequencies. But it cannot be held responsible for a beat of the correlation function or for the slight overall decrease in time which is often observed experimentally.

The correlation function method is characterized by a time scale which ranges between 10^{-14} to 10^{-13} s, and hence is ideally suited to study ultrafast molecular processes. Intramolecular vibrational energy transfer frequently takes place on a slower time scale (10^{-13} - 10^{-12} s or more). However, FRs can sometimes bring about fast transfers which can be detected by the present method. Although the information contained in the correlation function is strictly identical with that contained in the original optical spectrum, there is definite advantage in carrying out the Fourier transformation. The correlation function is more sensitive and can detect resonances which would remain unnoticed in the optical spectrum (compare fig. 5 of the present paper with fig. 3 of ref. [24]). Moreover, the parameters of the FR can be determined with a greater accuracy. Finally, the information is displayed in a much more suggestive way as a true intramolecular kinetic process.

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References

- [1] E.J. Heller, *J. Chem. Phys.* 68 (1978) 2066; 68 (1978) 3819.
- [2] E.J. Heller, *Accounts Chem. Res.* 14 (1981) 368; in: *Potential energy surfaces and dynamics calculations*, ed. D. Truhlar (Plenum Press, New York, 1981) p. 103.
- [3] E.J. Heller, E.B. Stechel and M.J. Davis, *J. Chem. Phys.* 71 (1979) 4759; 73 (1980) 4720.
- [4] S.Y. Lee and E.J. Heller, *J. Chem. Phys.* 71 (1979) 4777; D.J. Tannor and E.J. Heller, *J. Chem. Phys.* 77 (1982) 202.
- [5] A.J. Lorquet, J.C. Lorquet, J. Delwiche and M.J. Hubin-Franskin, *J. Chem. Phys.* 76 (1982) 4692.
- [6] D. Dehareng, B. Leyh, M. Desouter-Lecomte, J.C. Lorquet, J. Delwiche and M.J. Hubin-Franskin, *J. Chem. Phys.* 79 (1983) 3719.
- [7] J. Pollard, D.J. Trevor, J.E. Reutt, Y.T. Lee and D.A. Shirley, *J. Chem. Phys.* 81 (1984) 5302; J.E. Reutt, L.S. Wang, J.E. Pollard, D.J. Trevor, V.T. Lee and D.A. Shirley, *J. Chem. Phys.* 84 (1986) 3022.
- [8] J.E. Reutt, L.S. Wang, Y.T. Lee and D.A. Shirley, *J. Chem. Phys.* 85 (1986) 6928.
- [9] B. Rušić, *J. Chem. Phys.* 85 (1986) 3776.
- [10] H. Köppel, *J. Chem. Phys.* 77 (1983) 359.
- [11] D. Dehareng, *J. Chem. Phys.* 110 (1986) 375; 120 (1988) 261.
- [12] S.Y. Lee and S.K. Lim, *J. Chem. Phys.* 88 (1988) 3417.
- [13] D. Dehareng, *J. Chem. Phys.* 84 (1984) 393.
- [14] J. Brickmann and P. Russegger, *J. Chem. Phys.* 75 (1982) 5744; J. Brickmann, *J. Chem. Phys.* 78 (1983) 1884.
- [15] F. Duschinsky, *Acta Physicochim. URSS* 7 (1937) 551.
- [16] Y.B. Band and K.F. Freed, *J. Chem. Phys.* 63 (1975) 3382.
- [17] H. Kupka and O.E. Polansky, *J. Chem. Phys.* 80 (1984) 3153; H. Kupka and G. Olbrich, *J. Chem. Phys.* 80 (1984) 3163; 82 (1985) 3975.
- [18] C. Manneback, *Physica* 17 (1951) 1001.
- [19] F.T. Chau, *J. Mol. Struct. THEOCHEM* 151 (1987) 173.
- [20] E.J. Heller, *J. Chem. Phys.* 62 (1975) 1544; 65 (1976) 1289.
- [21] R.B. Walker and R.K. Preston, *J. Chem. Phys.* 67 (1977) 2017.
- [22] M. Bixon and J. Jortner, *J. Chem. Phys.* 77 (1982) 4175.
- [23] J.H. Frederick, E.J. Heller, J.L. Ozment and D.W. Pratt, *J. Chem. Phys.* 88 (1988) 2169.
- [24] M.J. Hubin-Franskin, J. Delwiche, P. Natalis, G. Caprace and D. Roy, *J. Electron Spectry.* 18 (1980) 295.