Time-resolved photoelectron angular distributions as a map of rotational motion

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Abstract

We discuss the application of photoelectron angular distributions as a probe of time-evolving rovibrational wavepackets. A physical picture is drawn of the mechanism through which rotation–vibration coupling mechanisms are reflected in the time-dependent photoionisation asymmetry parameters. The effects of complicating features that may obscure the interpretation of time-resolved photoelectron spectroscopies, including the field intensity and the inherent complexity of ionisation processes are examined. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

A substantial amount of experimental and theoretical work over the past few decades has established the role of time-resolved pump–probe spectroscopies [1–3] as an important complement to the more traditional, energy-resolved spectroscopies. Time-resolved photoelectron spectroscopy [4,5], in particular, is promising to share the advantages of energy-resolved photoelectron spectroscopy [6], both being spectroscopies of electronic configurations that are nevertheless directly sensitive to vibrational dynamics.

The information that can be extracted from time-resolved probes is greatly enhanced if one is able to resolve the signal with respect to one or more properties. Thus, while techniques that measure the integrated signal versus the pump–probe time delay (for instance total fluorescence spectroscopy or total mass spectrometry) reflect the dominant energy spacings composing the wavepacket, those that resolve the signal with respect to one or more properties (e.g. dispersed fluorescence [1] or translational energy spectroscopy [7]) provide more detailed information about the wavepacket dynamics, which translates into information about the underlying Hamiltonian. In the context of time-resolved ionisation spectroscopies, recent work has illustrated the possibilities of mapping wavepacket vibrations [8,9], of following in time energy transfer between coupled vibrational modes [10], and of observing the course of internal conversion [11–15] and intersystem crossing [16] in large polyatomic systems by resolving the photoelectron energy.

Femtosecond time-resolved photoelectron angular distributions (PADs) may be expected to provide a useful complement to the, by now established, energy-resolved technique [8–16]. In the CW domain [17–19,39,40] and in nanosecond experiments...
[20,21] the ability of electron angular distributions to provide structural information that is silent in angle-integrated observables has been clearly demonstrated [17–21,39,40].

In Ref. [22] we developed a nonperturbative scheme for computing photoelectron angular and energy distributions in femtosecond pump–probe studies and suggested the type and quality of information that could be extracted from such measurements. A first, fully nonperturbative application is given in Ref. [23]. More recently three independent experimental groups have reported the first measurements of PADs in femto- [24,26] or pico- [25] second-resolved experiments. At present several other groups are setting up similar experiments [27] and one expects a rapid development of the field in the next couple of years. It is, thus, timely for theoretical research to consider both new applications of time-resolved PADs and possible complications that may obscure the interpretation of future experiments.

Two different phenomena which are expected to be advantageously studied with time-resolved PADs were identified; electronically nonadiabatic or spin–orbit induced processes (internal conversion or intersystem crossing, often referred to collectively as nonradiative transitions), and coupling mechanisms that modify the rotational composition of the wavepacket. In the first case, PADs are expected to complement photoelectron energy distributions in the sense that the latter rely on energetic differences between the coupled states [15], while the former rely on their symmetry differences [28]. Here, change of the PAD with time results from the changing character of the electronic wavefunction. The study of such phenomena is, thus, primarily interesting in the case of large polyatomic systems, where internal conversions and intersystem crossings are the rule. The second phenomenon, the change with time of the rotational composition of a wavepacket due to strong field effects or rotation–vibration coupling, can be studied using time-resolved photoelectron spectroscopy only by resolving the photoelectron angle. In this case time-dependence of the PAD reflects the nuclear, rather than the electronic dynamics. Rotation–vibration energy transfer being a very general phenomenon to which only few observables are sensitive [20,25,29,30], it is of both formal and practical interest to study its effect on simple systems, where the essential physics can be readily extracted and system-dependent details are largely eliminated.

The first of the aforementioned phenomena is studied in detail in Ref. [28], where we extend the formalism of Ref. [22] to arbitrary polyatomic molecules, develop an approximate scheme for computing the observable in large systems and provide, based on symmetry arguments, criteria for choosing systems that will exhibit a change of the PAD upon internal conversion or intersystem crossing. The second phenomenon is addressed in the present work.

Turning to the complicating aspects of time- and angle-resolved photoelectron spectroscopy, we first note that femtosecond experiments in the gas phase are nearly always carried out at high laser intensities [22,31,32], a feature which has been often neglected in theoretical modelling of such studies. The brief duration of femtosecond pulses implies that modest powers translate into large intensities (a 0.1 mJ pulse with 1 mm beam diameter and 100 fs duration has an intensity above $10^{11}$ W cm$^{-2}$). Furthermore, ionisation is a complicated dynamical process, often involving resonances, coupled ion channels and complex interaction of the departing electron with the core. One may, thus, doubt the utility of such an involved process as a probe of the wavepacket evolution; ideally the probe process should serve as a template, rather than introduce its own dynamics. It is, thus, germane to consider both strong field effects that may interfere with the interpretation of future measurement and the extent to which the ionisation dynamics can be disentangled from the wavepacket dynamics that is being probed.

Below we first (Section 2) investigate the effect of the pump and probe intensity on the measured signal [23]. In Section 3 we study the effects of rotation–vibration coupling on the wavepacket dynamics and its reflection in time-resolved PADs. We conclude Section 3 (Section 3C) with a discussion of the possibility of circumventing the complex and often unknown ionisation dynamics in utilising time-resolved PADs as a probe. The final section summarises our results. Since the formalism required for computing photoelectron angular and energy distributions has been published elsewhere [22], we
focus throughout on the qualitative physics and on illustrative results. The present paper is, thus, not self-contained and readers interested in the theory may need to refer to the literature [22,28,33].

2. The role of the laser intensity

2.1. The evolving alignment of rovibrational wavepackets

As discussed in the Introduction, PADs are sensitive primarily to the rotational composition of wavepackets, i.e., to their alignment (we consider here electronically adiabatic dynamics — see Ref. [28] for the case where the electronic symmetry is the prime factor). The initial rotational composition is determined by the pump duration and intensity. In the weak field limit, the excited wavepacket is composed of the three rotational branches allowed in a 1-photon transition. In a nonperturbative field, the system undergoes Rabi-type cycles between the two near-resonant electronic states, exchanging another unit of angular momentum with the field on each transition [22,32]. The degree of rotational excitation is determined either by the pulse duration or by the balance between the intensity and the detuning from resonance. In the former case, \( J_{\text{max}} \), the maximum rotational level significantly populated, is roughly the number of cycles the system has time to make during the pulse; \( J_{\text{max}} \sim \frac{\tau}{\Omega_{R}} \), \( \tau \) being the pulse duration and \( \Omega_{R} \) the Rabi coupling. In the latter case, \( J_{\text{max}} \) is restricted by the requirement of sufficient intensity to overcome the accumulated detuning from resonance; \( \Omega_{R} \sim J_{\text{max}} \), the detuning, \( \Delta' \) growing roughly as \( J(J+1) \) [32]. Depending on the system it may or may not be possible to eliminate rotational excitation by decreasing the intensity such that \( \tau < \Omega_{R}^{-1} \). On the other hand, rotational excitation may be desirable, since rotationally broad wavepackets can be induced to align along a given axis or in a given plane [32,34].

A useful measure of the rotational composition of a wavepacket and the associated alignment is the expectation value of \( \cos^2 \theta \) in the wavepacket, where \( \theta \) is the angle between an axis fixed in the molecule and an axis fixed in space. In the classical limit (the limit of a broad rotational wavepacket) \( <\cos^2 \theta> \) describes the motion of the molecular axis in the space-fixed frame.

Fig. 1 shows a rovibrational wavepacket of NO(\( \Delta \Sigma \)) molecules during and subsequent to excitation from the ground \( \Pi \) state with a linearly polarized pump field. The pulse is assumed Gaussian with a 100 fs temporal width, centred about \( t_0 = 200 \) fs. Since NO is atypical in that in addition to being light it has weak Frank Condon overlaps and transition dipole elements, we choose an unrealistically high pump intensity (\( 5 \times 10^{14} \) W cm\(^{-2} \)). Similar effects to those described here would typically be observed at much lower intensities. Panel (a) shows the probability density of the rotational wavepacket during the first 500 fs. Panel (b) shows the expectation values of \( J \) and of \( \cos^2 \theta \) during and after the

![Fig. 1. Time evolution of a \( \Delta \Sigma \) NO rovibrational wavepacket during a linearly polarised pump pulse. (a) Time probability density as a function of time and the angle between the NO axis and time laser polarisation vector. (b) Time expectation value of \( \cos^2 \theta \) (solid curve) and the square root of the expectation value of \( J' \) (dashed curve) in the wavepacket, providing average measures of the degrees of alignment and rotational excitation, respectively.](image-url)
pulse, for a period of 3 ps. Subsequent to a transient oscillation during the turn-on, as the molecular axis begins to respond to the field, $\langle \cos^2 \theta \rangle$ drops well below the isotropic value of 1/3, corresponding to the alignment of the molecule (panel a) perpendicular to the polarisation vector. A corresponding increase of the rotational content, $\langle J \rangle$ is shown as a dashed curve. After the turn-off the rotational composition of the wavepacket is constant, with $\langle J \rangle \approx 5$, but the relative phases of the rotational components evolve; the molecular axis dynamically aligns parallel to the polarisation axis and $\langle \cos^2 \theta \rangle$ oscillates with a mean value well above the isotropic value of 1/3. The noticeable peak at 2250 fs in Fig. 1b is a signature of post-pulse alignment enhancement, a general phenomenon in the evolution of rotational wavepackets whose origin is unravelled by means of an analytical theory in Ref. [34].

On the time-scale of Fig. 1, the rotational composition of the NO($A^3\Sigma$) wavepacket is not affected by rotation–vibration coupling. Hence, the time evolution of $\langle \cos^2 \theta \rangle$ under field free conditions results merely from dephasing and revivals of the rotational components and is periodic in time, with a period commensurate with the rotational level spacing composing the wavepacket. In the classical limit the wavepacket is peaked in the forward–backward directions (with a corresponding peak of $\langle \cos^2 \theta \rangle$) at each multiple of the rotational revival time $T_{rev,rot} \pi / B_e$. This corresponds to periodic motion of the molecular axis with respect to an axis fixed in space at the classical period $\pi / B_e$. The alignment described in Fig. 1 is monitored in the next section by a photoionising probe.

2.2. Monitoring alignment: time- and angle-resolved photoelectrons

Fig. 2 shows the PAD obtained following ionisation of the wavepacket described in Section 2.1 as a function of the pump–probe time delay ($\Delta t$) and the polar angle between the field and the photoelectron scattering vector ($\theta_k$). The probe intensity is low, $1.4 \times 10^9$ W cm$^{-2}$, and its pulse duration is 100 fs.

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Fig. 2. Calculated photoelectron angular distribution (PAD) obtained by probing the $A^3\Sigma$ NO wavepacket with a $1.4 \times 10^9$ W cm$^{-2}$ pulse of 100 fs duration. $\Delta t$ is the time delay between the centres of the pump and probe pulses amid $\theta_k$ is defined with respect to the laser polarisation vector.
The overall p-shape of the PAD is expected since the ΩΣ state is strongly Rydberg in character, with the outmost electron occupying an s-orbital; the ionisation dipole elements thus ensure that the l = 1 partial wave of the electron dominates. This overall shape is of little interest from the viewpoint of time-resolved spectroscopy since it does not vary with time and conveys no information about the wavepacket dynamics. The periodic modulations marked in Fig. 2 reflect the periodic structure of <cos²θ> discussed above and their time scale is determined by the rotational composition of the wavepacket, i.e. by the rotational level spacings dominating the motion.

Fig. 3 shows the Δ dependence of the PAD at θk = 0 and compares it with a PAD obtained at a probe intensity of 1.4 x 10⁹ W cm⁻². The reader is referred to Ref. [23] for a complete discussion and for more detailed illustrations. We note here only that the PAD mimics faithfully the time evolution of the averaged alignment and that the probe intensity plays essentially no role within the range studied here, which we chose within and somewhat above the range typical of time-resolved photoionisation spectroscopy [22,31,32]. The insensitivity of the θk-dependence of the signal to the probe intensity is owing to the fact that the probe pulse hardly modifies the rotational composition of the wavepacket (the molecular property to which the PAD is sensitive). The field does not distort the wavepacket alignment since its intensity is insufficient to induce Rabi cycling between the neutral excited state and the ionisation continuum. In the absence of resonances such cycling requires significantly higher intensities, sufficient to compete with the rapid ionisation process.

3. Rotation–vibration coupling

In general, rotation–vibration coupling may arise from (either or both) the dependence of the moments of inertia on the vibrational coordinates (often referred to as centrifugal coupling), and the cross-terms of the angular momenta of rotation and vibration (often referred to as Coriolis coupling) [35–37]. In order to focus on the essential physics and avoid mathematical details, we consider here the simplest example, that of centrifugal coupling in a diatomic molecule. We refer the reader to Ref. [33] for a general formulation and to Ref. [25] for an experimental study of a large polyatomic molecule.

3.1. Effects on the wavepacket evolution

In the absence of coupling between rotational and vibrational degrees of freedom, the system’s nuclear eigenstates take a product form and its eigenvalues are given as a sum of a vibrational and a rotational energy,

\[ E = E_v + E_r. \]

The time evolution of the rovibrational wavepacket exhibits in this limit four time scales which, due to the large disparity between vibrational and rotational level spacing, are generally well-separated. The fastest motion is vibration at the harmonic frequency \( \omega_v \), typical at the 10⁻¹³ s scale (10⁻¹⁴ s for the lightest molecule, H₂ and 1.5 x 10⁻¹³ s for the heavy I₂). The next is vibrational revivals, determined by the anharmonicity of the potential and taking place on a picosecond time-scale. Within a Morse approximation the energy eigenvalues are

\[ E = \omega_v(v + \frac{1}{2}) + \omega_x(x + \frac{1}{2})^2 \]

and hence the vibrational revival time is

\[ T_{rev,vib} = \frac{2\pi}{\omega_x}, \]

roughly 3 x 10⁻¹³ s for the example of H₂ and 5 x 10⁻¹¹ s for I₂. The fundamental rotational motion, \( t_{rot} = \frac{2\pi}{(E_r - E_f)} \), is typically slower at low levels of rotational excitation.
but its rate increases rapidly with rotational excitation, due to the linear dependence of rotational level spacing on \( J \). By contrast to the vibrational case, the rotational revival time, \( T_{\text{rev,rot}} \), is comparable to the fundamental motion, \( T_{\text{rev,rot}} = \pi/2B_e \) (\( B_e \) being the rotational constant), and ranges from \( 3 \times 10^{-15} \) s for \( \text{H}_2 \) to \( 5 \times 10^{-10} \) s for \( \text{I}_2 \). As discussed above (see Fig. 1), \( \langle \cos^2 \theta \rangle \) exhibits only the rotational time scales. In the absence of rotational perturbations it is thus modulated on a long time-scale, commensurate with the rotational level spacings, and periodic in \( \pi/B_e \).

If rotation–vibration coupling is present, the system eigenvalues include a coupling term,

\[
\mathcal{E}^{vJ} = E^v + E^J + E^{vJ}
\]  

(for a diatomic molecule) and hence the wavepacket exhibits an additional time-scale. Typically, \( E^{vJ} \) is small compared with both vibrational and rotational level spacings; hence the coupling appears as a slow envelope in the time evolution of \( \langle \cos^2 \theta \rangle \), on a time-scale of \( T_{\text{RV}} = 2\pi/E^{vJ} \), large compared with the rotational period. This is shown in Fig. 4 for a wavepacket evolving on the \( A^1\Sigma \) state of \( \text{Na}_2 \), subsequent to excitation from the ground \( X^1\Sigma \) state with a 20 fs pulse. To simplify the dynamics we have chosen the pump duration to allow significant population in only rotational components \( J=0,2 \) of the ground and \( J=1,3 \) of the excited state.

At short times, \( \Delta t \propto E^{vJ} \ll 1 \), the effect of the coupling is not observed and the expectation value of \( \cos^2 \theta \) behaves as in a separable system. With only two rotational components, the wavepacket oscillates...
at the fundamental rotation time scale; \( t_{rot} = 2\pi / (E_j - E_f) \approx 30 \text{ ps} \) for Na\(_2\)\((A^1\Sigma)\) at the excitation level considered. In the general case the beat pattern exhibits several frequencies and is periodic only in the rotational revival time, \( T_{rot,rev} = \pi / B_0 \approx 150 \text{ ps} \). In the nearly classical limit of a rotationally broad wavepacket only the full revivals can be discerned [38].

As \( \Delta t \) becomes comparable to the coupling time constant, \( T_{\text{rev}} = 2\pi / E^{\alpha/\beta} \), the rotational components of the wavepacket dephase and the oscillation amplitude decays. Provided, however, that coherence is not lost, the rotational components gradually rephase and at integer multiples of \( T_{\text{rev}} \) the wavepacket is reconstructed. On a long time-scale, the oscillations at \( T_{rot,rev} \) are thus modulated by a slow envelope whose time constant is determined by the coupling strength.

The dephasing of the rotational components of the wavepacket on the coupling time-scale can be regarded as a result of the different rotational constants that are experienced by different vibrational levels. Equivalently, it can be understood as a consequence of the different centrifugal potentials which vibrational sub-wavepackets with different \( J \) experience.

### 3.2. Consequent photoelectron angular distributions

In this subsection we proceed to describe the mechanism through which the evolving rotational composition of the wavepacket, the result of rotation–vibration coupling, is reflected in the PADS. It is convenient to assume first that the electronic ionisation dipole elements (the matrix elements of the dipole operator connecting the bound and continuum electronic wavefunctions) are independent of the internuclear distances. This assumption is not essential to the theory [33], and the effect of relaxing it is discussed in the next subsection. Under this condition it is readily shown [33] that in the absence of rotation–vibration coupling the differential cross section takes a product form,

\[
\sigma(\theta_i | \Delta t) = \theta_{\text{vib}}(\Delta t) \sigma_{rot}(\theta_i | \Delta t).
\]  
(2)

As any pump probe signal, \( \sigma(\theta_i | \Delta t) \) oscillates with \( \Delta t \) on a time-scale commensurate with the level strengths. Dependent asymmetry parameters. In the weak field limit terms beyond \( \beta_{\text{J}}P_{\text{J}} \) vanish. The cylindrically symmetric form, Eq. (3), applies to the case of common linear polarisation of both pump and probe fields. For our present purpose, it is sufficient to consider the lowest order asymmetry parameter, \( \beta(\Delta t) = \beta_{\text{J}}(\Delta t) \). From the foregoing discussion it is clear that, in the absence of rotation–vibration interaction, Eq. (2), all the vibrational time-dependence is contained in the total cross section so that the asymmetry parameter \( \beta(\Delta t) \) is a smooth, slowly varying signal, which responds only to the alignment.

In the presence of rotation–vibration interactions the factorisation Eq. (2) breaks down and an additional time scale, \( T_{\text{rev}} = 2\pi / E^{\alpha/\beta} \) is introduced. At the start of the time evolution, \( \Delta t \ll T_{\text{rev}} \), the rotational components are in phase and the minor phase factor \( \Delta t E^{\alpha/\beta} \) is not noticeable. Hence \( \langle \cos^2 \theta \rangle \) and \( \beta(\Delta t) \) reflect solely the rotational motion. As \( \Delta t \) approaches the coupling time scale the different \( J \) components of the wavepacket gradually dephase. Consequently the short time, classical-like oscillation of the averaged alignment decays and fine structure appears in \( \beta(\Delta t) \). The structure is periodic in \( \Delta t \) with period \( t_{\text{vib}} = 2\pi \omega_v \) since the PAD probes the wavepacket within a restricted Franck–Condon window; the signal peaks each time the vibrational wavepacket traverses the Franck–Condon region. The vibrational structure disappears as the rotational components rephase and reappears periodically, as expected for a coherent
signal. While the rapid oscillations exhibit a trivial time scale (that of the fundamental vibration), the beat envelope of $\beta(\Delta t)$ follows the beat pattern of $\langle \cos^2 \theta \rangle$ and measures directly the strength of the rotation–vibration coupling.

A quantitative illustration of the picture drawn schematically above is given in Fig. 5, which shows the time evolution of $\langle \cos^2 \theta \rangle$ and $\beta$ for the Na$_2$X'\Sigma \rightarrow A^1\Sigma \rightarrow X^2\Sigma$ system. Panels (a) and (b) illustrate the early stage of the evolution, $\Delta t B^{\text{rot}} \ll 1$. At this stage the rotational components of the wavepacket dephase and revive due to essentially only the nonlinearity of the rotational spectrum. Consequently $\langle \cos^2 \theta \rangle$ exhibits practically only the rotational time scales, and vibrational structure in $\beta$ is barely noticeable. Panels (c) and (d) illustrate a later stage of the evolution, $\Delta t \approx \frac{1}{2} T_{\text{RV}}$, at which the rotational components are precisely out of phase, the oscillation amplitude of $\langle \cos^2 \theta \rangle$ has decayed to a minimum, and the structure in $\beta$ is fully developed. On longer time scales vibrational structure appears periodically at $\Delta t = (k + \frac{1}{2}) T_{\text{RV}}$, disappearing at $\Delta t = k T_{\text{RV}}$, as the initial condition is restored.

### 3.3. Effect of coordinate and photoelectron energy dependence in the photoionisation transition dipole moment

A major concern in the application of ionisation spectroscopies as a probe of wavepacket motions is the complicated nature of ionisation processes. This is particularly true when angular distributions are the observable; in the CW domain the sensitivity of the PAD to the details of the ionisation dynamics was clearly demonstrated [19,39,40]. If the dependence of the electronic ionisation amplitudes on the internuclear distances and the photoelectron energy, were to play a major role in determining the time depen-

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![Figure 5](image-url)  
**Fig. 5.** Time evolution of the alignment $\langle \cos^2 \theta \rangle$ [panels (a) and (c)] and the asymmetry parameter $\beta$ [panels (b) and (d)] for the Na$_2$, X'\Sigma \rightarrow A^1\Sigma \rightarrow X^2\Sigma$ system. Panels (a) and (b) illustrate the short time dynamics, where the effect of the coupling is hardly discernible. Panels (b) and (d) show a later stage of the evolution, at which time rotational components have dephased and the structure in $\beta$ is fully developed.
dence of the P AD, its value as a probe of the wavepacket evolution would be very limited.

The qualitative arguments and numerical results presented in the previous subsections were based on the assumption that the electronic ionisation amplitudes are independent of both the nuclear coordinates and the electron energy. It is, thus, important to investigate the extent to which coordinate or photoelectron energy dependency of the electronic ionisation amplitudes may obscure the reflection of rotation–vibration coupling in the observable. Only a qualitative discussion is given in this section so as to avoid the presentation of formulae. A quantitative numerical study is given in Ref. [33].

As shown in Fig. 5, the effect of rotation–vibration coupling is to introduce vibrational fine structure into $\beta$, whose amplitude beats with period $2\pi/E^{v,J}$. Mathematically this structure results from the breakdown of the factorisation in Eq. (2), which, in turn, is caused by the presence of a coupling term, $E^{v,J}$ in the eigenvalues and hence a phase $\exp(-iE^{v,J}\Delta t)$ in the cross section. Physically this structure results from deviation of the rotation of the molecular axis from that in a separable system.

It is clear that dependence of the electronic ionisation amplitudes on nuclear coordinates would lead similarly to breakdown of the factorisation Eq. (2) and hence to structure in the asymmetry parameter. In this case, the structure would arise solely from the nature of the probe and convey no information about the wavepacket motion. Nevertheless, the beating envelop of $\beta(\Delta t)$ can only arise from a coupling term in the energy eigenvalues. Coordinate dependence of the ionisation amplitudes leads to a time-independent coupling of the rotational and vibrational parts of the cross section. It, thus, introduces a constant background of vibrational fine structure into $\beta$, but does not change the beating pattern at $2\pi/E^{v,J}$, which measures the strength of the rotation–vibration coupling.

4. Conclusions

Our goal in the work described above has been to present a simple physical picture of the mechanism through which time-resolved photoelectron angular distributions map the evolving alignment of rovibrational wavepackets and, hence, probe coupling mechanisms that affect rotations. We focussed on time qualitative physics, omitting the formal and technical details. To conclude we briefly summarise our main findings:

1. A convenient and physically meaningful measure of the rotational composition of wavepackets is the expectation value of $\cos^2 \theta$. In the classical limit, the limit of a rotationally broad wavepacket, $\langle \cos^2 \theta \rangle$ describes the motion of the molecular axis with respect to an axis fixed in space. Exhibiting only the rotational coherences, $\langle \cos^2 \theta \rangle (\Delta t)$ is sensitive solely to the rotational motion, thus extracting from a multiple time-scale rovibrational wavepacket the information sought. In the absence of coupling of rotations with electronic or vibrational modes, $\langle \cos^2 \theta \rangle$ oscillates on a time-scale commensurate with the rotational level spacings dominating the wavepacket, and is periodic in the rotational revival time $\pi/B_r$. In the presence of coupling it exhibits a beat pattern whose envelope is determined by the coupling strength.

2. Time-resolved P ADs reflect the time-evolution of $\langle \cos^2 \theta \rangle$, being sensitive to the rotational composition of the wavepacket. For many purposes it is advantageous to consider the time evolution of the lowest order asymmetry parameter which follows the evolution of $\langle \cos^2 \theta \rangle$. In particular, in the presence of rotation vibration couplings, $\beta(\Delta t)$ exhibits a beat pattern whose envelope measures directly the coupling strength.

3. The pump intensity plays, in general, a significant role in femtosecond experiments. In the case that P ADs are the observable, the main effect to be considered is rotational excitation induced by the pump field. Rotational excitation can be often avoided, by choice of the pump duration. On the other hand it is an interesting phenomenon which may also carry practical benefit, e.g., as a means of aligning molecules.

4. The probe intensity does not modify the shape of the P AD within the range of relevance, see, however, Ref. [23] for a complete discussion.

5. The dependence of the electronic bound-free transition dipole elements on the nuclear coordi-
nates does not obscure the reflection of rotation–vibration coupling in the PADs.

References