Chemical Physics Letters 673 (2017) 103–107

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Line space theory of Resonant Four-Wave Mixing: New prospects for all-optical studies of photofragment states

A.P. Kouzov [a,*], P.P. Radi [b]

[a] Department of Physics, Saint-Petersburg State University, Ulyanovskaya str. 3, Peterhof, Saint-Petersburg 198504, Russia
[b] Paul Scherrer Institute, 5232 Villigen, Switzerland

ARTICLE INFO

Article history:
Received 5 July 2016
In final form 6 February 2017
Available online 8 February 2017

ABSTRACT

Based on the line-space quantum formalism, the potential of Resonant Four-Wave Mixing spectroscopy as a new tool to study rotational and translational anisotropy of photofragments produced by absorption of plane-polarized photons is theoretically addressed. Synergy of the flexible polarization setup, fine quantum state resolution and of the possibility to study translational recoil distributions, makes the tool unsurpassed among the all-optical means to interrogate the photofragment states. It allows to directly separate signals induced by the rotational anisotropy which remain silent in the most of laser-induced fluorescence responses and thus opens new ways to study rotational helicity, a crucial signature of the photolysis pathway.

1. Introduction

Reaction microdynamics, “the heart of chemistry” [1] manifests in the properties of nascent particles, which offers thereby considerable scope to track the reaction pathway. Quantum mechanically, reactions obey the inseparability principle [2] so that the product particles, such as fragments produced by photodissociation, can not be found in pure states, but should be described in terms of the density matrix ρ_S [3], the key consequence of the path. Evidently, the more we know about the measurable correlation characteristics of ρ_S (known as bipolar state moments [4]), the more definitely it can be inferred how a photon breaks a hitherto stable molecule. The states of the nascent particles are most directly accessed by spectroscopic techniques whose proficiency becomes unexcelled when a reaction itself is initiated by light [5]. An advent of the laser-induced fluorescence (LIF) techniques that occured about 40 years ago led to a first breakthrough in the photodissociation studies. The frequency- and polarization-resolved LIF spectra allow to directly monitor the directional properties of the angular momentum (**j**) of the product states [6] and provide detailed Doppler patterns [7] of the recoil velocity **v**, its correlation with **j** , and - according to Dixon’s theoretical picture [4] - a number of the double and triple correlations of **v** and **j** [8,9] with the dissociating transition dipole moment μ_{fi} of the parent molecule. Such vector correlations are direct consequences of the photodissociation path [5,10–14] and serve as a touchstone for intuitive bond rupture models as well as impetus to progress in the photoreaction scattering theory, the forefront topics in chemical physics. Especially intriguing is an effect of the photofragment handedness (helicity) characterized by a nonvanishing mean value of $\langle(\mathbf{v},\mathbf{j})\rangle$. In a wider sense, the helicity can be also associated with other correlations between the products of the first powers of **v** and **j** and the orientational characteristics of $\mu_{\mathbf{fi}}$. To our knowledge, direct evidences of the rotational handedness of molecular photofragments obtained with plane-polarized photolysis lasers are still missing although such LIF studies revealed that **v** and **j** in some cases are strongly aligned. To prove the helicity, i.e. the predominance of the clockwise rotation around the recoil direction over the counterclockwise one, or *vise versa*, additional experimental arguments should be found. More simply, such findings would imply that the rototranslational motion of a certain amount of the nascent particles resembles that of bullets from rifle’s barrel. The latest advances in the photolysis studies are due to tandems of optical spectroscopy and time-of-flight mass-spectrometry implemented in the Resonantly Enhanced Multi-Photon Ionization (REMPI) devices which allow to produce 2D- and 3D-images of photofragment recoil velocity distributions (see, e.g., the review [15]) on which the **v**-**j** correlations are imprinted. REMPI spectroscopy, especially linked with kinetic energy analysis of the resulting photoelectrons, continues to make enormous contributions to understanding of the photolysis mechanisms. Using REMPI, the electronic angular momenta orientation [16] (of Cl atoms produced at the ICl laser photolysis) and the atomic spin polarization (of H^{2}S photofragments [17,18]) were detected for the first time. As was theoretically shown [12], the

---

* Corresponding author.
E-mail address: alex@ak1197.spb.edu (A.P. Kouzov).

http://dx.doi.org/10.1016/j.cplett.2017.02.008
0009-2614/

helicity can arise either because of the interference between the electronic pathways when two or more dissociating continua with different symmetries are excited, or because of the excitation of a perpendicular vibronic transition.

However, the potential of much simpler, purely optical means is far from being exhausted. New LIF schemes exploiting circularly polarized dissociation and counter-propagating pump beams were theoretically explored by Alexander [19,20] and then introduced to practice. In so doing, not only the atomic polarization [21,22] of the HCl photofragments was detected but the first data on the rotational helicity of the OH radicals produced at the 355 nm photolysis of hydrogen peroxide [19] were obtained as well.

Among other all-optical devices, Resonant Four-Wave Mixing (RFWM) spectroscopy should be named for its unique characteristics making it a novel, suitable tool to photolysis studies. To generate a RFWM signal beam at $\omega_4 = \omega_1 - \omega_2 + \omega_3$, three input laser beams (1, 2, and 3) [23] are focused into a small volume at a specially designed geometry. The signal beam is as coherent and well collimated as the input beams and can be, therefore, fully captured by a detector, in contrast to spontaneous emission collection in LIF. Its intensity I_4 is proportional to the squared modulus of the third-order susceptibility $\chi^{(3)}$ and is tremendously enhanced when the input frequencies are tuned to molecular dipole-allowed transitions. Owing to such enhancement, RFWM was successfully used [24,25] to derive scalar characteristics of photolysis products at number densities as low as $10^{12}\ \mathrm{cm}^{-3}$. These pioneering studies generated considerable interest and, though detection of the finer anisotropic effects remained then problematic, a review of the day [26] optimistically predicted that the RFWM technique "will prove very sensitive to angular-momentum polarization" and that it "will be applied to the probing of anisotropic angular momentum distributions, adding another valuable optical technique to the more commonly used LIF and REMPI methods." Indeed, RFWM has four controllable polarizations whereas LIF possesses only two and, even when operating with plane-polarized beams, all angular-momentum moments of order L with $0 \leqslant L \leqslant 4$ are feasible for RFWM while only even-order moments ($L = 0, 2, 4$) can be tested by LIF at the same conditions. The separation of the laboratory-frame $L = 1$ term can be principally achieved by LIF with elliptically polarized beams [27,28] though at the expense of the setup complication. Anyway, the helicity derivation requires a next step - the Doppler-shape spectral analysis - which, to our knowledge, has not been done.

The $L = 1$ moment is far directly accessed by RFWM whereas the relevant Doppler shapes are obtained by merely scanning the input frequency. Also, the RFWM responses are automatically state-resolved, both for the one- (or Degenerate FWM operating between a pair of molecular states) and Two-Color (TC, involving three states) variants while such resolution in the conventional LIF setup requires a spectrometer. In contrast to LIF, REMPI and DFWM, the use of the double-resonance TC-RFWM techniques immensely enhances the spectral selectivity allowing to resolve congested spectra [29] which is especially important for studies of molecular photofragments. Another RFWM distinction from LIF and REMPI is that the channels contributing to the on-resonance susceptibility $\chi^{(3)}_{res}$ are interfering, an intrinsic RFWM feature which can markedly show up in the integrated intensities and shapes alike.

Apart from the overall setup simplicity, RFWM as compared to REMPI gains also in the polarization device flexibility that allows to directly separate signals due to the orientational anisotropy of $\mathbf{j}$. However, the REMPI velocity images contain much richer information than the RFWM Doppler shapes which are determined by the mean value of $\mathbf{v}$(see below). We notice also that RFWM is an efficient tool not only for molecular beams but for *in situ* measurements as well whereas REMPI applies solely to collisionless media. To summarize briefly, both techniques seem to complement each other to some extent.

So far, the DFWM [30,31] and TC-RFWM [32–34] theory has been completed only for the rotationally isotropic states. The first theoretical and experimental DFWM studies of the anisotropy induced by optical pumping were undertaken by Vaccaro and coworkers [35–38]. Very recently, DFWM [39] has been used for the first time to detect the anisotropy of the OH radicals at the H_2O_2 photodissociation by a plane-polarized radiation at 266 nm and to separate the $L = 1$ components whose spectral shapes were indicative of the OH helicity [40]. The further progress is plagued by the lack of an exhaustive theory. To fill the gap, we provide in this Letter a theoretical groundwork for the RFWM probing of photofragments. In so doing, the conventional weak-field approximation [30–34,41] is exploited.

The key issue is the derivation of $\chi^{(3)}_{res}$ which fully accounts for the rotational and translational anisotropy of nascent particles. To this end, the line-space (LS) Liouville formalism is the most appropriate tool which allowed a rigorous account for the collisional relaxation and proved thereby its superiority [33,34] over the conventional approaches [30–32] to isotropic systems. Advantageously, the LS derivations are done in a controllable, step-by-step manner which substantially facilitates cumbersome algebra in the anisotropic case. They are naturally combined with the irreducible spherical tensors (IST) machinery [42], a powerful tool to decouple different tensorial characteristics from $\chi^{(3)}_{res}$. As a result, the latter is converted into a sum of weighted products of the field, reaction path and molecular characteristics, i.e., into the form optimal for comparison with measured intensities.

2. Photofragment density matrix

The key input characteristics of the photolytic $f \leftarrow i$ transition are the excess $\Delta\varepsilon$ of the photon energy above the dissociation threshold and μ_{fi} which, taken together, determine the reaction path. The detected RFWM intensity I_4 depends on the unit polarization vector $\mathbf{e}_D$ (hereafter assumed to be plane-polarized) of the photolysis laser and on the polarization states of the input and signal beams. Besides, the effect of the $\mu_{fi} - \mathbf{v} - \mathbf{j}$ correlations on the signal shapes is to be elucidated as well as the behavior of I_4 vs the set of $\{J_k\}$ of the angular momentum quantum numbers of the resonant states.

The LS consists of quantum operators $A, B, \ldots$ acting on the photofragment states with the metric $\langle\langle A|B\rangle\rangle = Tr\rho_0 A^{\dagger}B$defined with the help of the isotropic part ρ_0 of ρ_S. The orthogonal and normalized LS basis consists of the symmetry-adapted $n \leftarrow m$ transition operators $K^{(L)}_Q(m,n)$ which are ISTs of rank L [42]

$$K^{(L)}_Q(m,n) = \rho_{mm}^{-1/2} \sum_{M_m M_n} (-1)^{J_m - M_m} C^{LQ}_{J_n M_n J_m - M_m} |\alpha_n J_n M_n\rangle\langle\alpha_m J_m M_m| \qquad (1)$$

Here, (α_k, J_k) denotes a set of the principal quantum numbers corresponding to the state $k(= m,n); J_k$ and M_k are the quantum numbers of the total angular momentum and its projection onto the OZ axis in the laboratory frame (LF); $C^{a\alpha}_{b\beta c\gamma}$ is the Clebsch-Gordan coefficient, and ρ_{mm} is the diagonal element of ρ_0. In what follows, we assume ρ_S to be diagonal with respect to α and J, but not to M; therefore, ρ_S can be expanded in $K^{(L)}_Q(m,m)(\equiv N^{(L)}_Q(m))$. To incorporate the velocity anisotropy, the LS basis vectors should be multiplied by $C^{(L)}_{\sigma}(\Omega_v)$, the Racah harmonics depending on the orientation Ω_v of $\mathbf{v}$ in LF (X, Y, Z). Since ρ_S is invariant under rotations of LF, it can be written as a linear combination of the conventional scalar products [42] (denoted by $(\ldots,\ldots)$) of two ISTs of the same rank (λ), i.e.,