

Photodissociation by Circularly Polarized Light Yields Photofragment Alignment in Ozone Arising Solely from Vibronic Interactions

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We present a direct determination of photofragment alignment produced by circularly polarized light in photolysis of a planar polyatomic molecule. This alignment arises via a new mechanism involving coherent excitation of two mutually perpendicular in-plane transition dipole moment components. The alignment is described by a new anisotropy parameter γ'_2 that was isolated by a unique laser polarization geometry. The determination of the parameter γ'_2 was realized in ozone photolysis at 266 nm where dc slice images of O(¹D₂) atomic fragments were acquired. A model developed for interpretation of the photolysis mechanism shows that it can exist only in case of failure of the Born-Oppenheimer approximation when electronic and vibrational (vibronic) interactions have to be taken into account. This finding suggests that determination of the alignment parameter γ'_2 can be used as a key for direct insight into vibronic interactions in photolysis of polyatomic molecules. The results obtained for ozone photolysis via the Hartley band showed significant γ'_2 alignment but little recoil speed dependence, consistent with the notion that, as opposed to the situation for derivative coupling, under our experimental conditions, the vibronic contributions to the nonadiabatic dynamics are not dependent on recoil speed.

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Vector correlations in photolysis of diatomic and polyatomic molecules have been intensively studied for many years [1–5]. The main vectors of interest are the transition dipole moment of the parent molecule μ , total molecular angular momentum \mathbf{J} , one fragment's recoil velocity \mathbf{v} , and angular momentum \mathbf{j} , that can be of rotational, electronic orbital, or spin origin. In particular, investigations of the vector correlations in photolysis reactions resulting in photofragment atomic orbital polarization were found to be very useful for understanding excited state dynamics in the molecular frame [5,6], revealing unique information on excited state symmetries, coherent excitation and dissociation mechanisms, and nonadiabatic processes [7–15] that cannot be obtained by other methods. The photofragment angular momentum polarization can be characterized by recoil-angle-dependent excitation cross-section matrix elements that are conveniently expressed by the fragment state multipole moments ρ_{KQ} of the rank K and component Q [16], where the $K = 0$ multipole describes the photofragment density, the $K = 1$ and other odd multipoles describe angular momentum orientation, and the $K = 2$ and even multipoles describe angular momentum alignment.

As suggested by Pitcheneyev *et al.* [17] the angular distributions of the fragment state multipole moments ρ_{KQ} in case of photolysis of any diatomic, or polyatomic molecule can be expanded in terms of the anisotropy parameters with the rank K : α_K , s_K , γ_K , γ'_K , and η_K . An alternative set of the polarization parameters $\mathbf{a}_q^K(p)$ was

suggested by Rakitzis and Zare [18] and generalized by Rakitzis and Alexander [19] for the case of photolysis of polyatomic molecules. As analyzed and tabulated by Shternin *et al.*, [13] these sets of parameters are equivalent to each other.

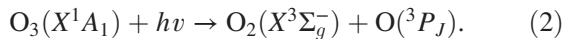
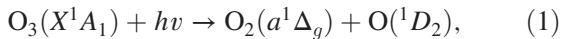
Up to now, most of the anisotropy parameters of the ranks $K = 1–4$ have been determined experimentally for photodissociation of a large number of diatomic and polyatomic molecules [9,10]. Although in the case of diatomic photolysis the relationship between the parameter values and the underlying photolysis dynamics is very well understood both on the qualitative (model) level and on the level of exact quantum mechanical computations, there are still many important open questions related to the interpretation of the anisotropy parameters in photolysis of polyatomic molecules even on the model level. In particular, no detailed mechanisms of atomic photofragment orientation or alignment in photolysis of a polyatomic molecule have been developed till now.

In this Letter we present for the first time experimental determination of the anisotropy parameter γ'_2 characterizing photofragment alignment produced by circularly polarized light. Furthermore, we show this arises via a new mechanism involving coherent excitation of two mutually perpendicular transition dipole moment components, and apply this in ozone photolysis at 266 nm. Although the mechanism was mentioned by Siebbeles *et al.* in their seminal paper [3], neither experimental nor theoretical

study of the effect has been carried out so far. As shown in this Letter, the parameter γ'_2 can be isolated from other sources of alignment by proper linear combinations of pump-probe laser geometries (see Supplemental Material [20] for details). A model developed for interpretation of the photolysis mechanism giving rise to γ'_2 in ozone photodissociation via the Hartley band shows that it can exist only in case of failure of the Born-Oppenheimer approximation in the excited \tilde{B} electronic state due to interaction between electronic and antisymmetric stretching vibrational motions. This finding suggests that the alignment parameter γ'_2 can be used as a key for direct insight into vibronic interactions. In particular, the γ'_2 value reflects the intensity of simultaneous excitation of two reaction channels related to antisymmetric and symmetric vibrations in the \tilde{B} electronic excited state and therefore can be used as a straightforward way for monitoring these excitation channels as a function of experimental conditions. Moreover, as the produced coherence behaves in a unique way in the vicinity of possible conical intersections, the γ'_2 parameter values contain information on nonadiabatic interaction occurring during photolysis and therefore can be used to probe these interactions as well.

Vector correlation studies for ozone photolysis using ion imaging were pioneered by Houston *et al.* [4,21]. They determined four of the five alignment parameters mentioned above using a full density matrix method. The results show the alignment has a tendency for enhanced population towards the $|m_j| = 0$ level, with little or no population in $|m_j| = 2$, thus suggesting alignment mainly from an incoherent parallel excitation mechanism. A more recent vector correlation investigation was reported for ozone photolysis at 266 nm by our group, by probing orbital orientation of the $O(^1D_2)$ product [22]. The results revealed strong orientation produced by linearly polarized light, indicating a significant contribution from simultaneous coherent excitation of parallel and perpendicular transition moment components to the dissociation.

Here we present a method utilizing an appropriate combination of pump-probe polarizations that permits isolation of the parameter γ'_2 by means of slice imaging, and apply this in ozone photolysis at 266 nm. Ozone was excited to the \tilde{B} diabatic electronic state that belongs to the $^1A'$ symmetry (1B_2 in C_{2v} symmetry group) at 266 nm; it then dissociated via two spin conserving channels shown in Eqs. (1) and (2) [23]. As is known, about 90% of the molecules follow pathway (1) and the rest, $\sim 10\%$, pathway (2) by crossing to the \tilde{R} state that belongs to the $^1A'$ symmetry (1A_1 in C_{2v} symmetry) [24]:



As can be shown on the basis of the general expressions for the photofragment state multipoles ρ_{KQ} [3,12], the parameter γ'_2 is related to the production of a photofragment state multipole off-diagonal component $\text{Im}[\rho_{21}]$ in the experimental geometry when circularly polarized probe light beam propagates along the X axis and the imaging detector is parallel to the XY plane [22,25]. The component $\text{Im}[\rho_{21}]$ was determined experimentally by a REMPI scheme with linearly polarized probe light according to the following signal intensity expression [13,26]:

$$I = I_0 \sum_K (Y_K(\mathbf{e}_{pr}) \cdot \rho_K) P_K, \quad (3)$$

where $K = 0-4$ is the multipole rank, \mathbf{e}_{pr} is the direction of the probe light polarization vector, $Y_K(\mathbf{e}_{pr})$ is a spherical harmonic, P_K is the line strength factor [26], and the term in parenthesis (\cdot) denotes the scalar product.

As can be shown using Refs. [3,12] and Eq. (3), the contribution to the fragment alignment from γ'_2 can be isolated through a differential image employing two orthogonal probe beam polarizations. The corresponding differential slice imaging signal can be presented in the form

$$\frac{I_{45} - I_{-45}}{\langle I_X \rangle + \langle I_Y \rangle + \langle I_Z \rangle} \approx -\frac{\sqrt{5} P_2}{4\pi P_0} V_2(j) \frac{\gamma'_2 \sin^2 \phi}{(1 - \frac{\beta}{8})}, \quad (4)$$

where I_{45} and I_{-45} are image signal intensities when the probe beam is linearly polarized at $\pm 45^\circ$ to the Z axis in the YZ plane, and the angle ϕ describes the signal distribution in the image (XY) plane. The terms $\langle I_X \rangle$, $\langle I_Y \rangle$, and $\langle I_Z \rangle$ are signal intensities with probe beam polarizations along the X , Y , and Z axes respectively, integrated over the angle ϕ . The constant $V_2(j)$ is given by $V_2(j) = 5\{j(j+1)/(2j+3)(2j-1)\}^{1/2}$, where j is the atomic fragment electronic angular momentum. The difference $(I_{45} - I_{-45})$ in the numerator in Eq. (4) cancels contributions from zeroth-rank state multipole ρ_{00} and alignment components ρ_{20} and ρ_{22} . The normalization factor in the denominator in Eq. (4) is proportional to the zero-rank component ρ_{00} (e.g., total photofragment number) neglecting orientation and alignment effects.

The dc slice [27] velocity map imaging configuration used in this Letter is schematically depicted in Fig. 1. In brief, a circularly polarized photolysis laser beam at 266 nm propagated along axis X and dissociated ozone molecules according to the reactions Eqs. (1) and (2). The probe laser beam propagated along the $-X$ direction and was linearly polarized at either 45° , or -45° to the Z axis. The resulting O^+ ions were mass selected and collected by the ion imaging system with the detector parallel to the XY plane. Ozone was produced by a commercial ozone generator and trapped in a silica gel trap at -78°C . The experiment was carried out by sending He carrier gas at 1 atm over the silica

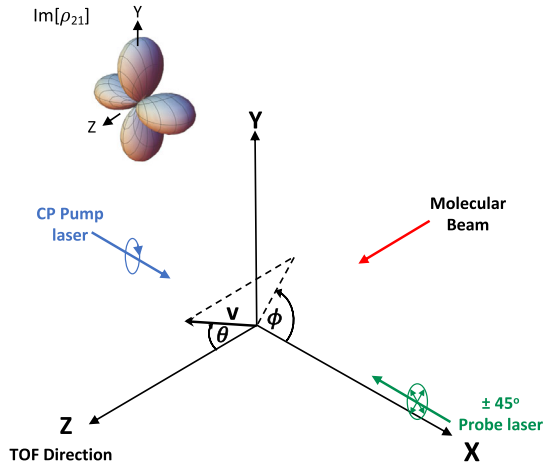
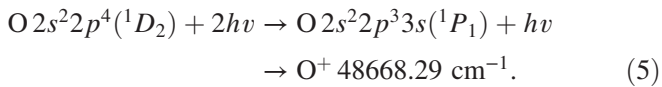


FIG. 1. Laboratory frame coordinate system. Inset is the alignment distribution arising from circularly polarized photolysis light, related to the γ'_2 from the $\text{Im}[\rho_{21}]$ state multipole.

gel while raising the temperature to -40°C . The gas mixture of ozone seeded in He then passed through a pulsed piezoelectric valve and the supersonically expanded molecular beam was skimmed prior to the interaction with counterpropagating laser beams. The experimental setup with the modified ion optics arrangement has reported in our previous work [28,29]. The photolysis laser beam at 266 nm was sent through a Glan Polarizer (Thor Labs GLB-10) to clean the linear polarization prior to producing circularly polarized light from a Berek's Polarization Compensator (New Focus Model 5540) set at quarter-wave retardation. The probe laser wavelength was chosen to selectively ionize the $\text{O}(^1D_2)$ photofragment through the 1P_1 state by 2 + 1 REMPI at 205 nm according to the following scheme,



The linearly polarized probe light polarization was varied using a Hinds Photoelastic Modulator (PEM-100), which enables the accurate switching of polarizations alternatively

without altering the power or position. The power of the pump laser on entry into the chamber was 0.4 mJ/pulse and the probe 0.1 mJ/pulse. Both lasers were focused to the interaction region by fused silica lenses ($f = 230$ mm).

The sliced images (symmetrized) taken with right circular polarized pump beam and with $\pm 45^\circ$ linear probe are shown in Fig. 2 along with the difference image. When right circular polarization of the pump beam was switched to left circular polarization, the difference image changed its sign. This observation evidently confirms that the photofragment alignment detected in our experiment resulted from mapping the photon helicity of the photolysis beam. The intensity distribution in the difference image is clear evidence that the alignment effect observed was due to the γ'_2 mechanism in agreement with Eq. (4). The images were analyzed using the finite slice analysis (FinA) program [30,31] developed in our group. The distinct rings in the image correspond to $\text{O}(^1D_2)$ production in conjunction with $\text{O}_2(a^1\Delta_g)$ vibrational levels 0–3. We measured the alignment anisotropy parameter γ'_2 associated with production of the distinct vibrational levels of the $\text{O}_2(a^1\Delta_g)$ cofragment by integrating the images across each vibrational peak and fitting to Eq. (4). The obtained γ'_2 values are presented in Table I. As can be seen in Table I, the recoil velocity dependence is not pronounced: all parameter values are almost the same within experimental error. We find the average value for β is 0.91, and it also shows a weak velocity dependence consistent with previous studies.

The mechanism of the photofragment orbital alignment produced in photolysis of ozone with circularly polarized light can be clearly understood on the basis of a set of the anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ introduced recently by Shternin and Vasyutinskii [12]. The anisotropy transforming coefficients are proportional to the anisotropy parameters $\alpha_K, s_K, \gamma_K, \gamma'_K, \eta_K$ in pairs, having an advantage that they are labeled by two additional quantum numbers k_d and q_k that refer to unique photolysis mechanisms. The quantum number k_d is the rank of the photolysis light polarization: $k_d = 0$ refers to an isotropic part of the light, $k_d = 1$ refers to the *helicity* of circularly polarized light, and $k_d = 2$ refers to the light polarization vector \mathbf{e}

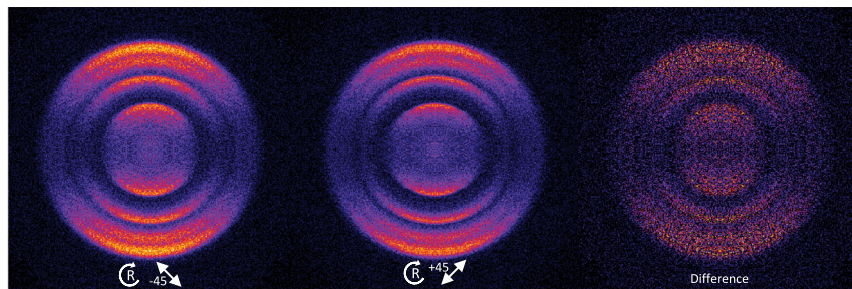


FIG. 2. dc sliced images acquired with indicated pump-probe polarizations and the difference image used for determination of the γ'_2 parameter. Right circular pump and $\pm 45^\circ$ probe.

TABLE I. Parameters obtained by fitting the difference image of Fig. 2 to Eq. (4), along with the range of possible values. Note the range is dependent on β , so it varies slightly with recoil speed.

Parameter	$v = 0$	$v = 1$	$v = 2$	$v = 3$
γ'_2	-0.040 ± 0.003	-0.053 ± 0.002	-0.039 ± 0.003	-0.045 ± 0.002
γ'_2 range	$-0.20 \dots 0.20$	$-0.21 \dots 0.21$	$-0.21 \dots 0.21$	$-0.19 \dots 0.19$

alignment. The quantum number q_k is the component of the ranks k_d and K ($\min\{K, k_d\} \geq q_k \geq -\min\{K, k_d\}$) onto the asymptotic recoil direction \mathbf{k} . Physically, the component q_k describes coherence between the polarization states of the photolysis light and between the polarization states of the outgoing photofragments: $q_k = q - q' = \Omega_k - \Omega'_k$, where q is a spherical component of the photolysis light polarization vector \mathbf{e} and Ω_k is a projection of the angular momentum \mathbf{J} , both onto the recoil direction \mathbf{k} . As shown by Shternin and Vasyutinskii [12], the quantum number q_k is preserved in any photolysis reaction. The rank $K = 2$ alignment is characterized by five independent anisotropy parameters, describing different types of incoherent and coherent excitation mechanisms [10]. The γ'_2 parameter is proportional to the \mathbf{c}_{11}^2 anisotropy transforming coefficient in the Shternin and Vasyutinskii nomenclature [12] and refers to coherent excitation with circularly polarized light. It holds quite different properties compared to other alignment parameters because it results from mapping the photon helicity of the photolysis light into the photofragment alignment.

A model illustrating the mechanism of the photofragment orbital alignment produced in photolysis of ozone with circularly polarized light is presented schematically in Fig. 3. (Note, this molecular frame coordinate system is distinct from the lab frame system described above.) The mechanism of γ'_2 production requires simultaneous excitation of the molecule with two mutually perpendicular laser electric fields E_y and E_z shown in Fig. 3. However, due to the symmetry of the ozone excited electronic state \tilde{B} ,

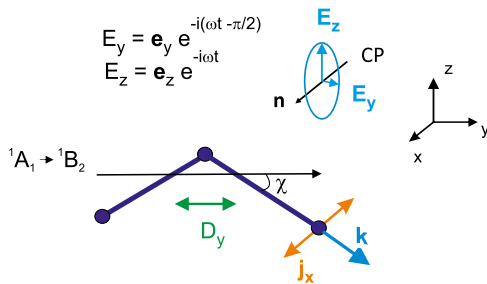


FIG. 3. Body frame model explaining production of photofragment orbital alignment with circularly polarized photolysis. The molecular plane is parallel to the yz plane and z is the molecular symmetry axis, \mathbf{k} is the recoil direction, D_y is the molecular electronic transition dipole moment, and j_x is the photofragment angular momentum aligned perpendicular to the molecular plane.

the transition dipole moment for the ${}^1A_1 \rightarrow {}^1B_2$ transition is parallel to the y axis. Therefore, the required condition cannot be fulfilled if one takes into account only the electronic contribution to the optical transition.

However, the condition can be fulfilled by considering vibronic interactions in the molecular excited state resulting in breakdown of the Born-Oppenheimer principle. In this case the symmetry of the total molecular wave function is built from the symmetries of the electronic and vibrational wave functions. In particular, the combination ${}^1B_2 \otimes {}^1a_1 = {}^1B_2$, where the term 1B_2 represents the electronic wave function symmetry, the term 1a_1 represents symmetric vibration, and the term \otimes denotes the irreducible product results in the 1B_2 total symmetry, where the transition dipole moment from the ground state is parallel to y axis in Fig. 3 [32]. At the same time the combination ${}^1B_2 \otimes {}^1b_2 = {}^1A_1$ where the term 1b_2 represents antisymmetric vibration results in the 1A_1 total symmetry where the transition dipole moment is parallel to the z axis in Fig. 3. Thus, simultaneous excitation of symmetric and antisymmetric vibrational modes in the excited state results in simultaneous excitation of two mutually perpendicular transition dipole moment components D_y and D_z as required for realization of the γ'_2 photolysis mechanism.

The coherent excitation leads to combined oscillation of the molecular optical electron along the y and z directions. However, the molecular electron oscillation in an inhomogeneous electric molecular field of the O-O bond causes an additional phase shift. Assuming that the oscillation amplitude along the direction z is described by the expression

$$A_z = A_0 \sin \omega t, \quad (6)$$

where ω is the photolysis light frequency, the oscillation amplitude along the y direction can, in general, be written in the form

$$\begin{aligned} A_y &= A_0 \sin(\omega t - \pi/2 + \xi) \\ &= A_0(-\cos \xi \cos \omega t + \sin \xi \sin \omega t), \end{aligned} \quad (7)$$

where the phase $-\pi/2$ is the phase shift between the E_y and E_z electric field components in Fig. 3 and ξ is the phase shift that depends of the details of the molecular electric field distribution.

As can be seen in Eq. (7) the amplitude A_y in general contains two terms: one of them is in phase with the

amplitude A_z and another is in quadrature with it. The in-phase term of the amplitude A_y together with the amplitude A_z result in oscillation of the molecular optical electron along a certain direction in space that depends on the phase shift ξ and leads to the $O(^1D_2)$ fragment angular momentum alignment observed in our experiment. The alignment direction is perpendicular to the molecular plane as shown in Fig. 3.

Note that an alternative explanation of the coherent effect related to γ'_2 could be simultaneous excitation of the ozone \tilde{B} and \tilde{A} electronic states from the ground state as these states already have the required 1B_2 and 1A_1 symmetries in C_{2v} molecular geometry. However, according to the computations of Schinke and McBane [33] the cross section of direct photoexcitation of the \tilde{A} state from the ground state at 266 nm is about 10^{-6} times smaller than the \tilde{B} state absorption cross section and therefore this dissociation mechanism can be neglected. Thus, the relatively large anisotropy parameter γ'_2 values shown in Table I manifest an important role of vibronic interaction in dissociation via the \tilde{B} excited state of ozone. According to the model presented in this Letter, the quadrature term in Eq. (7) together with the amplitude A_z in Eq. (6) result in a circular oscillation trajectory of the optical electron that can give rise to angular momentum orientation of the $O(^1D_2)$ fragment in the direction perpendicular to the molecular plane. The effect is described by the anisotropy parameter γ_1 that has been probed by Lee *et al.* [22]. The comparison of γ'_2 and γ_1 experimental values can be used for determination of the important model phase shift ξ in Eq. (7) characterizing molecular electric field distribution. Rough comparison of the result in this Letter with that reported by Lee *et al.* [22] suggests that the phase shift ξ at 266 nm is about $\xi \approx \pi/2$ as the γ_1 value reported by Lee *et al.* [22] was close to 0.

The model described above is quite simplified; however it is based on the results of the recently developed quantum mechanical theory describing vector correlations in photolysis of planar polyatomic molecules with polarized light [34]. The expression for the anisotropy parameter γ'_2 given by the quantum mechanical theory can be presented in the form

$$\gamma'_2 \propto \text{Im}[\langle \Psi_{\text{fin}}^{(1)} | d_1 | \Psi_g \rangle \langle \Psi_{\text{fin}}^{(2)} | d_0 | \Psi_g \rangle^*], \quad (8)$$

where terms in angular brackets are transition dipole moment matrix elements, Ψ_g is an initial molecular ground state wave function, $\Psi_{\text{fin}}^{(1)}$ and $\Psi_{\text{fin}}^{(2)}$ are final photofragment wave functions related to two interfering reaction channels, and d_q with $q = 1, 0$ are molecular dipole moment spherical components onto the molecular axis. Lee previously reported a profound speed dependence for the γ'_1 parameter [22] from linear photolysis polarization. This velocity dependence, absent for γ'_2 , shows that the wave

function amplitudes and phases for the two excitations differ for circular vs linear photolysis polarization owing to differing excitation mechanisms. These differences are the subject of ongoing investigations.

According to the results of the quantum mechanical treatment [34], the γ'_2 parameter value is also very sensitive to photolysis mechanism, in particular to possible non-adiabatic interactions in conical intersection areas. The theoretical approach mentioned above and the conclusions made for the ozone molecule can be readily generalized to other tri- and polyatomic molecules. The general experimental procedure for the γ'_2 parameter determination in all cases is the same as that described above. Depending on the molecular structure, this mechanism can result in simultaneous population of two excited states of different symmetry related to two different reaction channels. The γ'_2 parameter value is proportional to the product of two transition dipole moment matrix elements in Eq. (8) calculated for each reaction channel. The transition dipole moment matrix elements depend on all molecular dynamics including molecular rotation during photolysis, bending motion, and possible nonadiabatic interactions. Therefore, the γ'_2 can be used for monitoring of these reaction channels and dynamics as a function of experimental conditions.

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