Stereodynamics of Photon-induced Reactions via Doppler-resolved Laser-induced Fluorescence Spectroscopy: Photodissociation of HONO₂ and the Reaction of O(¹D) with CH_4

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The application of polarised, Doppler-resolved laser-induced fluorescence (LIF) probing of the products scattered from photon-induced 'half-collision' (photodissociation) and 'full-collision' (bimolecular reaction) processes is developed to include the velocity dependence of their stereodynamics. Fourier-transform inversion procedures are used to derive the products' speed distributions W(v') and vector correlations $\beta_{ij}(v')$ (a) in the photodissociation of HONO₂ and (b) in the bimolecular reaction of O(¹D) with CH₄. In the former example, they provide new insight into the stereodynamics of the photodissociation

$$HONO_2 + hv \rightarrow HO(v = 0, N) + NO_2(\tilde{X}, \tilde{A})$$

In the latter, together with newly developed LAB \rightarrow CM simulation methods, they provide new insight into the stereodynamics of the reaction

$$O(^{1}D) + CH_{4} \rightarrow OH(v = 4, N) + CH_{3}$$

The OH is shown to be generated with its rotational angular momentum \mathbf{j}' , constrained to lie in a plane directed perpendicular to its centre-of-mass relative velocity, \mathbf{k}' .

1. Introduction

The measurement of reagent and product vector correlations lies at the heart of any stereodynamical study of atomic or molecular collisions.¹ There are two generalised strategies for such measurements:² crossed beam (or beam-gas) studies in which product velocity distributions are measured either via angle-resolved time of flight, or via polarised, Dopplerresolved optical (laser) probing. The latter strategy has the advantage of being product quantum state selective. If a laser beam is substituted for one of the molecular beams, the strategies allow the study of photodissociative, half-collisions rather than full, bimolecular collisions. In the last year or so, a new variant has been developed, which exploits the understanding of photodissociative dynamics, and uses molecular photodissociation to generate a well characterised 'beam' of reactive and/or energetic fragments, whose subsequent collisions can be studied using polarised, Doppler-resolved laser probe techniques.³⁻⁵ This new approach, velocity-aligned photofragment dynamics, offers the attraction of studying 'molecular beam' collisions under bulb conditions, allowing a greatly enhanced sensitivity of product detection in quantum state selected levels.

The purpose of this paper and its companion⁶ is to demonstrate the enormous power of polarised, Doppler-resolved LIF probing, particularly when combined with Fouriertransform direct inversion procedures,^{6–8} in projecting a stereodynamic view of both photodissociation and bimolecular collisions. This is based on the analysis of Dopplerresolved spectra recorded under different polarization and photolysis-detection geometries to allow determination of linear and angular momentum correlations, scalar product pair correlations, speed distributions and quantum state distributions. Sections 2 and 3 provide a summary of the experimental and analytical methods; Section 4 demonstrates their application to the stereodynamics of a model photodissociation,⁹

$$HONO_2 + hv \to HO(v, N) + NO_2 \tag{1}$$

and a model reactive collision

$$O(^{1}D) + CH_{4} \rightarrow OH(v \leq 4, N) + CH_{3}$$
(2)

proceeding through an 'insertion' mechanism. Its stereodynamics contrast with those of the stripping reaction reported earlier.⁵ r

$$O(^{1}D) + N_{2}O \rightarrow NO(v \ge 16, N) + NO(v = 0, N)$$
(3)

Their application to a model non-reactive collision system

$$HO(v = 0, N) + Ar, He \rightarrow HO(v = 0, N') + Ar, He$$
 (4)

will be presented in a subsequent communication.¹⁰

2. Experimental

The laser photolysis-probe systems have been described elsewhere.⁵ All experiments employed an excimer pumped, etalon-narrowed, polarised dye laser to probe the nascent products of photodissociation or bimolecular reaction. The etalon-narrowed linewidth was 0.04 cm⁻¹ (undoubled). In the photodissociation experiments, the excimer laser also pumped a second, frequency-doubled dye laser, to provide a polarised photolysis beam at 280 nm.⁹ The differing optical paths introduced a photolysis-probe delay of *ca.* 10 ns; this delay ensured collision-free conditions, given a total pressure in the flowing gas scattering cell of ≤ 13 Pa.

In the bimolecular collision studies the velocity-aligned reagents $O(^{1}D)$, were generated by polarised excimer photolysis of N₂O (ArF at 193 nm). The OH(v, N) fragments, generated by reaction of $O(^{1}D)$ with CH₄¹¹ were probed via polarised LIF detection through the OH(A \leftarrow X) transition. Nascent conditions were ensured by maintaining pressures ≤ 16 Pa and delay times in the range 100–200 ns.

Experiments were conducted with both parallel and perpendicularly aligned laser polarisation vectors, and coaxial and perpendicular photolysis-probe laser beam geometries, in order to determine the contributions made by the various velocity-dependent vectorial angular anisotropies to the observed contours of Doppler-resolved LIF spectral lines. Velocity-averaged rotational alignments of nascent OH fragments, referenced to the collision vector k [the (j', k) correlation measured by the bipolar moment $\beta_{k, j'}$] were also determined from the integrated relative spectral intensities of individual LIF features recorded using coaxial and perpendicular probe geometries.¹² These velocity-averaged rotational alignments were used to normalise each of the experimental Doppler profiles, which were then analysed through a direct inversion procedure⁶ to expose their velocity dependence (see Section 3).

3. Doppler Profile Analysis

The products of a molecular photodissociation or a bimolecular collision are, in general, scattered into a range of angles, velocities and quantum states. If the products are probed via LIF (or ionisation) detection, it is possible to determine (in principle) the distribution over their internal quantum states, but the Doppler-resolved spectral profiles of individually selected levels will be sensitive both to their speed distributions and to the alignments of their linear (velocity) and rotational (angular momentum) vectors. This dependence is expressed by the equation¹³

$$D(v'_{p}) = C \int_{v'=vp'}^{\infty} \frac{W(v')}{2v'} \left\{ g_{0}(v') + g_{2}(v')P_{2}\left(\frac{v'_{p}}{v'}\right) \right\} v'^{2} dv' \quad (5)$$

where v'_{p} is the component of velocity along the probe laser propagation vector

$$g_0(v') = b_0 + b_1 \beta_{kj'}(v')$$
(6a)

$$g_{2}(v') = b_{2} \,\boldsymbol{\beta}_{\boldsymbol{k}v'}(v') + b_{3} \,\boldsymbol{\beta}_{v'j'}(v') + b_{4} \,\boldsymbol{\beta}_{\boldsymbol{k}v'j'}(v') \tag{6b}$$

 $W(v')v'^2$ is the speed distribution of the scattered product, $\beta_{k'j'}(v')$, $\beta_{kv'}(v')$... represent the velocity-dependent bipolar moments of the product's vectorial angular distributions, and b_0, b_1, \ldots, b_4 are scalar coefficients with values which depend on the experimental probe detection geometry and the selected type of rotational transition (P, R or Q[†]).

In a molecular photodissociation experiment, $k \equiv \mu$, the transition dipole of the parent molecule and v' represents the recoil velocity of the probed fragment. In a velocity-aligned photofragment collision experiment, k represents the reagent collision vector (which is referenced to ε via the photofragment translational anisotropy, β) and v' represents the laboratory recoil velocity of the scattered product. The multipliers b_1 , b_2 and b_4 must also be multiplied by $\beta(k)/2$, where $\beta(k)$ represents the average anisotropy of the reagent collision vector.⁵

In both types of experiment, determination of the velocity dependence of the bipolar moments (*i.e.* the product vector correlations) has generally been avoided heretofore, by assuming an effective anisotropy, $\beta_{eff} \equiv g_2(v')/g_0(v')$ which is independent of the product velocity;¹³ however, the advent of Fourier-transform procedures for directly inverting the experimental Doppler profiles has now provided a means of directly determining the velocity-dependent moments (as well as the product velocity distribution itself); see the accompanying paper.⁶ Their separate determination is facilitated by taking appropriately weighted averages of normalised Doppler profiles recorded under alternative photolysis-detection geometries for selected P(N) [or R(N)] and Q(N) transitions.^{14†} This procedure enables individually chosen terms to be projected out of the expansions. Fourier-

transform inversion of the averaged profiles then allows determination of the speed distributions $W(v')v'^2$ and the speed dependence of each of the bipolar moments $\beta_{ij}(v')$.⁶ Velocity-averaged moments can also be determined via the definition

$$\langle \boldsymbol{\beta}_{ij} \rangle \equiv \frac{\int_0^\infty W(v') \boldsymbol{\beta}_{ij}(v') v'^2 \, \mathrm{d}v'}{\int_0^\infty W(v') v'^2 \, \mathrm{d}v'}$$
(7)

Despite these advances, the Doppler profile analysis of the products of bimolecular collisions (as opposed to unimolecular photodissociation) presents a problem: that of the LAB \rightarrow CM transformation for the product velocity vector correlations. The observed distribution of product speeds $W(v')v'^2$ reflects several contributing factors: the spread of reagent velocities, the dynamics (energy partitioning) of the reactive collisions and the CM differential cross-sections. Direct resolution of these contributions is not possible,¹¹ but it can be effected by an iterative backsimulation procedure based upon assumed trial differential cross-sections; see accompanying paper.⁶ It has proved possible, for example, to recover both the speed distribution, $W(v')v'^2$ and the LAB velocity dependence $\beta_{kv'}(v')$ of OH fragments scattered from the reaction of velocity-aligned $O(^{1}D)$ atoms with CH_{4} , by assuming an isotropic CM differential cross-section. Alternative assumptions, e.g. strongly directional sideways or backward-forward cross-sections are unsuccessful, see Section 4. Similar procedures can be employed to probe k', j' and k, k', j' correlations.

In the present application, random errors in the returned speed distributions arising from the fitting and inversion are rather small (see, for example, the dashed curves in Fig. 1, 2 and 5). This observation is consistent with the comparatively high signal-to-noise ratios of the input experimental composite Doppler profile data. Systematic errors are more difficult to assess, but one potential source arises from uncertainties in the laser linewidth estimated to be ca. ± 0.01 cm⁻¹. To ascertain whether the returned speed distributions and vector properties were sensitive to the choice of laser linewidth employed in the analysis, the data presented below have been refitted with a ± 0.01 cm⁻¹ variation in the width of the input laser lineshape function. In all cases the returned distributions were found to be insensitive to such changes, reflecting the fact that the experimental laser bandwidth was sufficient to resolve the important features of the Dopplerbroadened profiles and hence of the velocity distributions. A more detailed discussion of the testing of the data analysis procedures outlined here can be found in the accompanying paper.6

4. Results and Discussion

Photodissociation of Nitric Acid

In 1988, August *et al.*, using Doppler-resolved polarised LIF spectroscopy, were able to probe the stereodynamics of the photodissociation⁹

$$HONO_2 + hv(280 \text{ nm}) \rightarrow NO_2 + OH(v, N)$$

The OH fragments were generated predominantly without vibrational excitation, but carried a modest degree of rotation, estimated at 4.6% of the total available for distribution among the recoiling fragments. The majority of the energy was concentrated into the nascent NO₂ (*ca.* 65%), with the remainder appearing as photofragment translation.⁹ In order to estimate the translational energy disposal it was convenient to assume a Gaussian distribution (in energy) for the

[†] Table 1 of the companion paper⁶ summarizes the pump-probe geometries and weighting factors employed in constructing the composite Doppler profiles.

Table 1 Photodissociation of HONO₂ at 280 nm: mean energy disposals (cm⁻¹) among the primary products, OH(v = 0, N) and NO_2

N	E ^{OH} r	$ar{E}_{ ext{t}}^{ ext{OH}}$	$ar{E}_{t}^{\mathbf{NO}_{2}}$	$ar{E}_{ ext{INT}}^{ ext{NO}_2}$	$\Delta ar{E}_{ m INT}^{ m NO_2}$ a
1	126	4110	1518	13716	6500
	126	4200	1552	13590	6820
6	426	4241	1568	13325	6290 (fast component)
		ca. 700	ca. 260	ca. 18080	- (slow component)
8	792	4255	1576	12837	6850 (fast component)
		ca. 700	ca. 260	ca. 17720	- (slow component)

Data in italics refer to the estimates made earlier⁹ using indirect simulation procedures. The excess available energy is taken to be 19470 cm⁻¹. ^a FWHM of internal energy distribution in nascent NO₂.

function $W(v')v'^2$, the parameters of which were adjusted on an iterative 'trial and error' basis, until the best least-squares fit to the experimental Doppler profiles was obtained. Subsequent analysis yielded a set of velocity-averaged values for the set of bipolar moments ($\beta_{uv'}$, $\beta_{u'i'}$, $\beta_{v'i'}$ and $\beta_{uv'i'}$).

the set of bipolar moments $(\beta_{\mu\nu}, \beta_{\muj'}, \beta_{\nu'j'} \text{ and } \beta_{\mu\nu'j'})$. The advent of the Doppler lineshape analytical procedures, in particular the use of Fourier-transform inversion rather than spectral contour simulation, now permits a direct determination of the photofragment speed distribution, $W(v')v'^2$ and the velocity-dependent vector correlations, expressed by $\beta_{i,i}(v')$. These functions convey considerably more detailed dynamical information than the averaged values that were estimated through the earlier, more approximate analysis.⁹ A direct comparison between the two can be made by using eqn. (7) to redetermine the averages; they are displayed in Tables 1 and 2. The agreement between the two sets of values reflects the serendipitous choice of the assumed distribution function W(v'), in the simulation procedure. The derived distribution functions, obtained by direct inversion, together with the velocity-dependent moments are shown in Fig. 1-4; they include representative data for OH(N = 6, 8) and for OH(N = 1) (for which all the rotational vector correlations necessarily vanish).

Inspection of the figures, and the accompanying tables establishes several new dynamical and stereodynamical indicators: (1) The speed distribution functions for OH(N = 6, 8)appear to be bimodal, with a minor, 'slow' component peaking at $v' \approx 900$ m s⁻¹ and a major 'fast' component peaking at $v' \approx 2250$ m s⁻¹. The corresponding distribution function for OH(N = 1) only displays the 'fast' component.[†] (2) On the basis of energy conservation, the most probable internal energy of the nascent NO₂ molecules which accompany the recoiling OH(N = 6, 8) fragments is $ca. 13\,000 \text{ cm}^{-1}$ ('fast' recoil) or $ca. 18\,000 \text{ cm}^{-1}$ ('slow' recoil). (3) The translational vector correlations for OH(N = 6, 8) fragments, measured by the mean value of $\beta_{\mu\nu'},$ fall from $\langle\beta_{\mu\nu'}\rangle\approx+0.4$ to +0.5 for the 'fast' component, to $\langle \beta_{\mu\nu'} \rangle < 0$ for the 'slow' one; for OH(N = 1), the translational alignment remains effectively constant, with $\langle \beta_{\mu\nu'} \rangle \approx +0.23$. (4) The rotational vector correlation, $\beta_{v'J'}$ for OH(N = 8) also falls, from $\langle \beta_{v'j'} \rangle \approx +0.4$ for the 'fast' component, to near zero for the "slow' one.

Consider first, the bimodal velocity distribution of the OH(N = 6.8) fragments. Excitation at 280 nm is sufficient

(energetically) to access the two alternative dissociation channels: $OH(v = 0, N) + NO(\tilde{X}^2 A)$ (1a)

HONO₂ +
$$hv$$

OH($v = 0, N$) + NO₂($\tilde{A} \,^{2}B_{2}$) (1 b)

The simplest interpretation of the bimodal velocity distribution is to attribute the fast component to channel (1*a*) and the slow one to (1*b*). The assignment would imply the concentration of *ca*. 13 000 cm⁻¹ [NO₂(\tilde{X})] and *ca*. 8000 cm⁻¹ [NO₂(\tilde{A})] into rovibrational motion of the nascent NO₂ molecules; given the successive expansion and contraction of the equilibrium N—O bond lengths in the sequence HONO₂ \rightarrow HONO^{*}₂ \rightarrow HO + NO^{*}₂ and the changes in the NO₂ bond angles from 120 to 134° [NO₂(\tilde{X})]¹⁵ or 111° [NO₂(\tilde{A})],¹⁶ the high vibrational excitation is readily understood.

The electronically excited state accessed by photon absorption at 280 nm is associated with an $n \rightarrow \pi^*$ transition, populating the first excited singlet state, 1 ¹A". At first sight, this would imply a transition dipole directed perpendicular to the recoil axis and $\langle \beta_{\mu\nu'} \rangle < 0$; however the excited state is nonplanar, and the transition has a very low oscillator strength (2×10^{-6}) .¹⁷ A vibronically allowed transition into the ¹A' state can accommodate the apparent conflict, with the $NO_2(\tilde{X})/OH(N)$ fragments recoiling along a direction inclined at ca. 40° to the initial parent molecular plane.⁹ Channel (1b) is predicted to correlate with the second electronically excited singlet state of HONO₂, 2¹A".¹⁷ The associated electronic transition is considerably less forbidden $(f \approx 4 \times 10^{-5})$ but has its maximum intensity at ca. 220 nm (cf. 270 nm) and its origin at ca. 270 nm.¹⁷ Assuming the 'slow velocity' channel to be associated with (1b), and given the wavelength of the absorbed photon, 280 nm, the near-zero translational alignment for this channel is unlikely to be due to a balance between oppositely polarised overlapping transitions, accessing the 1¹A" (¹A') and 2¹A" states. Alternatively the nearzero alignment might be attributed to a slow predissociation path, but this is also very implausible given the totally struc-

Table 2 Bipolar moments reflecting the vector correlations in OH(v = 0, N) generated via photodissociation of $HONO_2$ at 280 nm

N	$\langle \beta_{\mu \nu'} \rangle$	<β _{µ<i>j'</i>} >	$\langle \beta_{v'j'} \rangle$		<β _{µv' J'} >
1	0.23	n/a	n/a	n/a	
	0.16	n/a	n/a	n/a	
6	0.40	not det	not determined		(fast component)
	0.44	0.18	0.29	0.21	
	<0	not det	ermined		(slow component)
8	0.53	0.21	0.38	-0.10	(fast component)
	0.40	0.18	0.52	-0.14	· • /
	< 0		<i>ca</i> . 0	—	(slow component)

Data in italics refer to earlier estimates⁹ assuming no product velocity dependence and employing indirect spectral simulation procedures.

[†] Inspection of the shapes of the raw Doppler profile data [see Fig. 1(a), 2(a) and 2(b)] confirms that the slow OH(N = 6, 8) component is genuine and not an artifact of the inversion procedure. Note that the profile for OH(N = 1) is comparatively flat topped, indicative of the absence of slow recoiling OH(N = 1) fragments, whilst those for OH(N = 6, 8) display much more rounded structure around the line-centre. The vector correlations for the slow OH(N = 6, 8) component (see Fig. 3 and 4) are more difficult to quantify. However, it is clear from the data that the magnitude of all vector correlations falls dramatically (to close to zero) below a speed of *ca*. 1500 m s⁻¹, where the slow component becomes prominent in the corresponding speed distribution functions.



Fig. 1 (a) Composite Doppler profile (with fit and residuals) for OH(N = 1), generated via the photodissociation of $HONO_2$ at 280 nm, and the inverted OH speed distribution, $W(v')v'^2$. Details of the pump-probe geometries and weighting factors employed in constructing the composite Doppler profiles are given in the accompanying paper.⁶ (b) Composite Doppler profile for OH(N = 1) and the velocity-dependent moment, $\beta_{\mu\nu}(v')$, obtained by Fourier-transform inversion and application of eqn. (7) (see text).

tureless character of the parent molecular absorption continuum. The most likely interpretation is recoil along directions 54.7° , close to the magic angle (cf. ca. 40° for the products of the 'fast' channel). This conclusion is consistent with Bai and Segal's potential-energy surface calculations.¹⁷ At extended HO-NO₂ distances they predict a considerably greater out-of-plane angle for the $2^{1}A''$, than the $1^{-1}A''$ surface. Access to the 'slow' channel (1b) could then be associated with a radiationless transfer from the $1^{1}A''$ to the $2^{1}A''$ surface as the excited molecule begins to dissociate.

Finally, consider the product rotational alignment, $\langle \mathbf{\beta}_{v'J'} \rangle$ for OH(N = 8) which also falls, from a value of +0.4 for the



Fig. 2 As for Fig. 1 but showing (a) composite Doppler profile (with fit and residuals) for OH(N = 6), generated via the photodissociation of HONO₂ at 280 nm, and the inverted OH speed distribution, $W(v)v'^2$. (b) As for (a) but for OH(N = 8).

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Fig. 3 As for Fig. 1(b) but showing composite Doppler profile for OH(N = 8) and the velocity-dependent moment, $\beta_{\mu\nu}(v')$, obtained by Fourier-transform inversion and application of eqn. (7) (see text)



Fig. 4 As for Fig. 1(b) but showing composite Doppler profile for OH(N = 8) and the velocity-dependent moment, $\beta_{ef}(v)$, obtained by Fourier-transform inversion and application of eqn. (7) (see text)

'fast' channel to near zero for the 'slow' one. Its magnitude is dictated primarily by the balance between the torsional and bending/impulsive contributions to the rotational angular momentum of the OH(N) fragments; a decrease in $\langle \beta_{v'l'} \rangle$ implies a relative increase in the bending/impulsive contribution, or a decrease in the torsional contribution. The increased out-of-plane motion of the dissociating HONO₂(2¹A") would certainly deliver a greater bending torque to the NO₂ but might be expected to have relatively little effect on the OH fragment (increased orbital angular momentum would sustain the conservation requirements). On the other hand, the absence of a 'slow' component in the speed distribution for OH(N = 1) does imply a higher level of rotational excitation in the OH fragments generated via channel (1b). A plausible explanation for the observed behaviour could be provided if there were an increased bending torque associated with changes in the O₂N-O-H angle following transfer onto the 2¹A" surface.

$O(^{1}D) + CH_{4} \rightarrow OH(v \leq 4, N) + CH_{3}$

In direct molecular photodissociation, the speed dependence of the bipolar moments $\beta_{ij}(v')$, is likely to be dramatic only when fragmentation proceeds via multiple electronic surfaces (e.g. in HONO₂). In contrast, the $\beta_{ij}(v')$ moments observed for photoinitiated bimolecular reactions will in general depend sensitively on v', particularly for reactions with broad product angular distributions. For such systems, extraction of the speed dependence of the bipolar moments and of W(v')itself (which will also be a sensitive indicator of the centre-ofmass k-k' distribution) is essential for the correct interpretation of the Doppler profile data: as illustrated below, interpretations based solely on the velocity-averaged moments can provide a very misleading picture of the collision dynamics.

Rovibrational populations in the OH fragments generated via the reaction

$$O(^{1}D) + CH_{\lambda} \rightarrow OH + CH_{3}; \Delta H_{0}^{\ominus} = -182 \text{ kJ mol}^{-1}$$

have been obtained by a number of workers.^{11,18} A significant fraction of the reaction exothermicity is channelled into OH internal excitation; population of vibrational levels, $OH(v \leq 4)$ has been observed following reaction with $O(^{1}D)$ generated by photolysis of O₃ at 248 nm.^{11,18} Whilst the OH product energy disposals are non-statistical, the reaction is believed to proceed via an insertion mechanism and the deep CH₃OH potential well probably has a profound influence on the reaction dynamics at low collision energies.¹¹

In the present study, $O(^{1}D)$ atoms have been generated via the photodissociation of N₂O at 193 nm, a process characterised in detail by Huber and co-workers using time-of-flight techniques.¹⁹ Based on their O(¹D) speed distribution and translational anisotropy ($\beta = 0.48 \pm 0.02$) it is possible to calculate the distribution of relative velocity vectors, k, and collision energies, as described previously⁵ and summarised in the accompanying paper.⁶ The resulting distributions are very similar to those for the $O(^{1}D) + N_{2}O$ reaction (see Fig. 1 of ref. 5b), with the velocity peaking at $k \approx 3000 \text{ m s}^{-1}$ and a full width at half maximum (FWHM) of 1500 m s⁻¹, corresponding to a mean collision energy of $ca. 36 \text{ kJ mol}^{-1}$. The translational anisotropy of the reagent relative velocity vectors, $\beta(k) \leq 0.48$, is approximately constant over the 2000- 4000 m s^{-1} range and takes an average value of *ca*. 0.45.

To illustrate the application of Doppler-resolved Fouriertransform spectroscopy to bimolecular reactions, the analysis is applied to the Doppler profiles recorded for the OH(v = 4,N' = 8) fragments, probed via the P₁(8) and Q₁(8) transitions of the A-X(1,4) band. This specific OH fragment has an internal energy of ca. 173 kJ mol⁻¹ and thus its production corresponds approximately to thermoneutrality. This serves to

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Fig. 5 Composite Doppler profile (with fit and residuals) for OH(N = 8, v = 4), generated by the photoinitiated reaction of O(¹D) with CH₄ and the inverted OH LAB speed distribution function, $W(v')v'^2$



Fig. 6 As for fig. 5, but showing the experimental data and inverted velocity-dependent moment, $\beta(k) \cdot \beta_{kv'}(v')$, where $\beta(k) \le 0.48$ (see text)



Fig. 7 As for fig. 5 and 6 but showing the data and inverted velocity-dependent moment, $\beta_{v', t'}$

restrict the CH₃ fragment, by energy conservation, to a relatively narrow distribution of internal energies, so simplifying the interpretation of W(v') and the bipolar moments. (Such a strategy would, of course, be unnecessary in the study of a triatomic reactive system).

Fig. 5-7 show the experimental data along with the fits, the inverted speed distribution, $W(v')v'^2$, and the bipolar moments, $\beta(k) \cdot \beta_{kv}(v')^{\dagger}$ and $\beta_{v',j'}(v')$. The velocity-averaged moments $\langle \beta_{i,j}(v') \rangle$ are given in Table 3 and have been calculated from the inverted distributions via eqn. (7), assuming a velocity-averaged value of $\langle \beta(k) \rangle \approx 0.45$.

We focus initially on the $\beta_{kv}(v')$ moment. A cursory inspection of its velocity-averaged value, $\langle \beta_{kv'} \rangle = 0.55$, implies an average angle between v' and k of ca. 33°. Given that the most probable product LAB speed is 1.8 km s⁻¹ (see Fig. 5) and the mean speed of the CM is $v_{cm} = 1.5$ km s⁻¹ a simplistic LAB-CM transformation would yield a CM product

Table 3 Velocity-averaged bipolar moments $\langle \beta_{ij} \rangle$ for OH (v = 4, N = 8) generated in the reaction of O(¹D) with CH₄; average reagent collision energy, $\langle E_{CM} \rangle = 36$ kJ mol⁻¹ and translational anisotropy ($\beta(k) \rangle = 0.45$

$\langle \beta_{kv'} \rangle$	<β _{kj'} >	<β _{v' j'} >	$\langle \beta_{kv'j'} \rangle$
$+0.55 \pm 0.05$	-0.15 ± 0.07	-0.13 ± 0.05	$+0.50 \pm 0.20$

[†] Note that separation of $\beta(k)$ and $\beta_{kv}(v)$ is possible only at the highest reagent velocities, where $\beta(k)$ tends to a limiting value of 0.48 ± 0.02 .²¹

speed, $w' = 980 \text{ m s}^{-1}$ and an average CM scattering angle (of k' with respect to k) close to 90°, *i.e.* preferential sideways scattering.

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This simplistic analysis is very misleading, however, as illustrated by the trial simulation of W(v') and $\beta(k) \beta_{kv'}(v')$ shown in Fig. 8. This employs an isotropic angular distribution of k' about k and assumes (i) a total reaction cross-section that is independent of |k| and (ii) a fixed CH₃ internal energy (ca. 800 cm⁻¹) such that production of OH(v = 4, N = 8) + CH₃ is approximately thermoneutral. Despite these approximations both the width of the W(v') distribution and the form of the strong dependence of $\beta_{kv'}$ on v' are well reproduced. (Details of the numerical integrations employed in the simulations are presented in the accompanying paper.⁶)

The conclusion that the OH fragments are scattered nearly isotropically in the centre-of-mass, (which is not surprising given that reaction at these collision energies probably pro-





Fig. 9 Simulations illustrating the sensitivity of the OH LAB speed distribution, $W(v')v'^2$ (b) and the moments $\beta(k) \beta_{kv'}(v')$ (c) and $\beta_{v'j'}(v')$ (d) to the different centre-of-mass differential cross-sections $(d\sigma/d\Omega)$ shown in (a).

Fig. 8 Comparison of the experimental (---) with the simulated (---) OH LAB speed distribution, $W(v')v'^2$ (a) and the bipolar moments $\beta(k) \beta_{kv'}(v')$ (b) and $\beta_{v'j'}(v)$ (c). The simulations assume an isotropic centre-of-mass angular distribution of k', about k (see text and the accompanying paper⁶ for more details).

ceeds via an intermediate CH₃OH collision complex¹¹) is reinforced by the alternative trial simulations presented in Fig. 9. These serve to illustrate the sensitivity of the W(v') and $\beta_{kv}(v')$ distributions to the assumed CM differential crosssection. Two features are of particular note: (i) narrow product angular distributions lead to sharp laboratory speed distributions, W(v'), and to $\beta_{kv'}(v')$ moments which vary little with v' (in contrast with the experimentally derived distributions) and (ii) forward and/or backward scattering in the CM is readily distinguished in the LAB frame by the different speed distributions and the $\beta_{kv'}(v')$ values. Such large variations in the laboratory speed distributions and vectorial properties would be readily observable in the raw experimental Doppler profile data. For example, the forward and backward speed distributions [numbered (ii) and (iv) in Fig. 9(b)] would lead to Doppler profiles with widths (full width at half maximum) of ca. 0.4 and 0.1 cm⁻¹, respectively. The profile associated with forward scattering would also display a more square topped structure than either that associated with backward scattering, or that observed experimentally (which has an FWHM ≈ 0.25 cm⁻¹).

The Doppler profile analysis also provides information on the product speed dependences of the bipolar moments which depend on j'. Significantly, both $\beta_{kv'}(v')$ and $\beta_{v'j'}(v')$ tend to their maximum possible values, +1 and $-\frac{1}{2} (\equiv v' \parallel k \text{ and } j' \perp$ v') for OH fragments travelling at the highest LAB speeds. These are associated not only with products from the highest reagent collision energies, but also with those OH fragments which are forward scattered in the CM frame, i.e. with $k'(||w')||k \ (\beta_{kv'} = +1)$ and $v' = |v_{cm} + w'|$. For these fragments, the (v', j') correlation provides direct insight into the $(\mathbf{k}', \mathbf{j}')$ correlation since \mathbf{v}' is necessarily parallel to \mathbf{k}' . Thus for the forward scattered OH products, with $\beta_{v'j'} \rightarrow -\frac{1}{2}$, j' must lie perpendicular to k'. At lower product LAB speeds $\beta_{v'l'}(v')$ decreases in magnitude and probably changes sign. Such behaviour is inconsistent with j' lying perpendicular to the collision plane (containing k and k'), since $\beta_{v'l'}(v')$ in this case would remain at its limit of $-\frac{1}{2}$ for all product speeds, v'. A satisfactory fit to the $\beta_{v'j'}(v')$ speed dependence can be obtained if j' is assumed to be cylindrically distributed about k', at a fixed angle close to 90° for all CM scattering angles [cf. Fig. 8(c)]. The speed dependence of $\beta_{v'j'}(v')$ therefore reflects the different projections of j' on v' as the CM scattering angle between k' and k varies. Analogous behaviour might be anticipated for the $\beta_{kj'}$ and $\beta_{kv'j'}$ moments; indeed, the observed signs and magnitudes of $\langle \beta_{kj'} \rangle \approx -0.15$ and $\langle \beta_{kv'j'} \rangle \approx 0.5$ are consistent with the observed (k', j') correlation.

5. Conclusions

Polarised, Doppler-resolved laser probing of the products of photon-induced reactions, both photodissociation (half-collision) and bimolecular (full-collision), provides a powerful route into the stereo-dynamics of molecular collisions, complementing the alternative strategy of angle-resolved, time-offlight analysis. The ability to unfold the velocity dependence of the products' vector correlations, and their speed distributions using direct inversion procedures has advanced the Doppler analysis method to the point where the two alternative strategies are directly, and beneficially competitive. The successful application of detailed Doppler profile analyses to a rapidly widening family of photon-induced reactions (as well as non-reactive collisions) and its further extension developed in the present work, surely demonstrate that the strategy has now reached maturity.

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