

## Final Report on EPSRC Grant no. GR/N20584

### Photochemistry of Hydride Radicals

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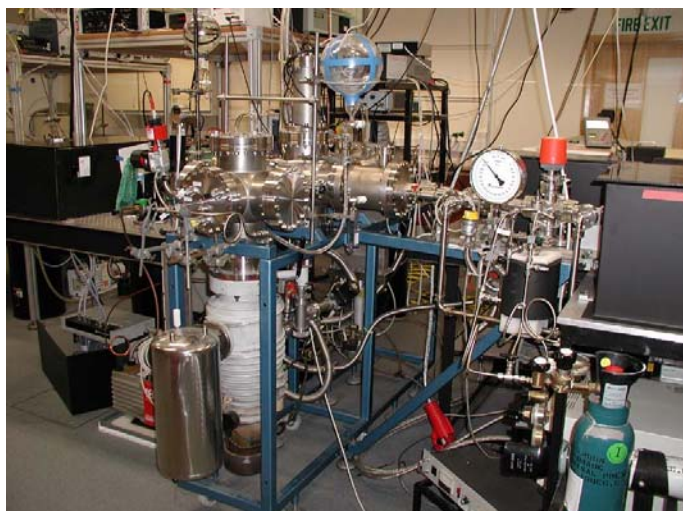
This small grant provided a project studentship, 7.25 man months of technical support and a consumables allocation of £16K to allow significant extension of an on-going programme of high resolution photofragment translational spectroscopy (PTS) experiments based on use of the H atom Rydberg tagging method.<sup>1</sup> The principles underlying H atom PTS are straightforward. A seeded molecular beam of the hydride of interest is photolysed, and the nascent H atom photofragments are 'tagged' *at source* by two colour two photon excitation to a Rydberg state with high principal quantum number,  $n$ . These Rydberg atoms have extremely long lifetimes. After tagging, the H atoms continue to recoil with a speed and angular distribution characteristic of the fragmentation process by which they were created. Those that fly in the direction of the detector are field ionised immediately prior to detection. Their time-of-flight (TOF) spectrum carries an imprint of the internal energy disposal within the (unobserved) partner fragment, without any of the attendant space charge blurring that limits the resolution of any PTS experiment where the product of interest is ionised at source, rather than after TOF separation. The aim of this application was to start a programme of work dedicated to studying the photofragmentation dynamics of jet-cooled hydride radicals, like CH<sub>2</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and C<sub>3</sub>H<sub>5</sub> (and their deuterated analogues), prepared by pulsed pyrolysis methods. The application proposed extensive redesign of the existing apparatus to allow characterisation and optimisation of the internally cold beam of the radical of interest by incorporating a purpose designed time-of-flight mass spectrometer around the interaction volume where the molecular beam is crossed by the counter-propagating laser beams used for photolysis and for the H atom tagging process.

In the event, a talented project student was appointed – Rafay Qadiri (a Bristol Chemical Physics graduate), the experiment was re-designed and reconstructed successfully, with much enhanced sensitivity, but the proposed work on hydride *radical* photolysis was put on hold for reasons explained below. Instead, several photodissociation studies of stable hydride molecules were undertaken during the grant period. Specifically, EPSRC quota funded student Phill Cook completed a very detailed series of experimental (and complementary theoretical) studies of the Lyman- $\alpha$  (121.6 nm) photolysis of H<sub>2</sub>S and D<sub>2</sub>S,<sup>2</sup> and of CH<sub>4</sub>, SiH<sub>4</sub> and GeH<sub>4</sub>,<sup>3</sup> as well as a detailed *ab initio* study of earlier experimental results we had obtained regarding the near ultraviolet (UV) photolysis of hydrazoic acid (HN<sub>3</sub>).<sup>4</sup> Rafay Qadiri was tasked with investigating the photofragmentation dynamics of several, related, 16 valence electron molecules – allene (H<sub>2</sub>CCCH<sub>2</sub>), propyne (CH<sub>3</sub>CCH)<sup>5,6</sup> and ketene (CH<sub>2</sub>CO).<sup>7</sup> Each of these studies yielded new, detailed photophysical data of a quality and precision far exceeding anything reported hitherto, and revealed significant errors and misconceptions in the previous scientific literature. The revisions to traditional thinking provoked by the allene and propyne work, in particular, is attracting interest within the combustion community. Both pre-doctoral students derived great benefit from the efforts of Leverhulme Trust funded post-doctoral research fellow Dr Emma Feltham, who also worked full-time on the experiment throughout the period 2000-2.

Before embarking on a detailed summary of the various results obtained it is first necessary to justify the significant change in project objectives. This was a direct consequence of our success in obtaining JIF funding for major refurbishment of not just the laser laboratories in which this experiment is housed (on South level 3) but most of the South Block building of the School of Chemistry. The (JIF funded) internal refurbishment was synchronised with University funded overcladding and refenestration of South Block. Though badly need, and much welcomed, the whole refurbishment process was hugely disruptive. Refurbishing the laser laboratories required that every single item be moved while the refurbishment progressed. The H atom PTS experiment is one of the largest apparatuses. It, and its two attendant laser tables and their contents, were out of action for the best part of 9 months throughout the period April-December 2001. The main refurbishment project carried on in other parts of South Block until late 2002, and services in particular remained 'erratic' until the summer of 2002. None of this came as a surprise, but student's development and progress had to be managed within this context. In the specific case of project student Rafay Qadiri, it was clear that he would have a six month window at the start of his Ph.D. during

which time experimental research could be expected to proceed as normal, then a ‘fallow’ period when the lab. would be inaccessible, and then another period of (hopefully) eighteen months to complete his Ph.D. Phill Cook was coming to the end of his Ph.D. by the time the JIF work started, and it proved no inconvenience whatsoever to have him concentrate on *ab initio* quantum chemical calculations of major portions of the potential energy surface (PES) for the first excited electronic state of  $\text{HN}_3$  – to complement experimental measurements he made in the early part of his Ph.D.<sup>8</sup> I made the decision that the careers of both Rafay Qadiri and Dr Feltham would be better served by their tackling a (seemingly) ‘easy’ experiment in the first six month period, during which time Rafay would master the experiment, and gain data that he could analyse and (hopefully) write up during the fallow period. This fallow period would also be the time for experimental re-design, and ordering of the necessary new parts. These plans worked – to a degree. Rafay Qadiri has now accumulated a sufficient body of experimental data and has embarked on writing his Ph.D. thesis that should be ready for submission in early 2004.

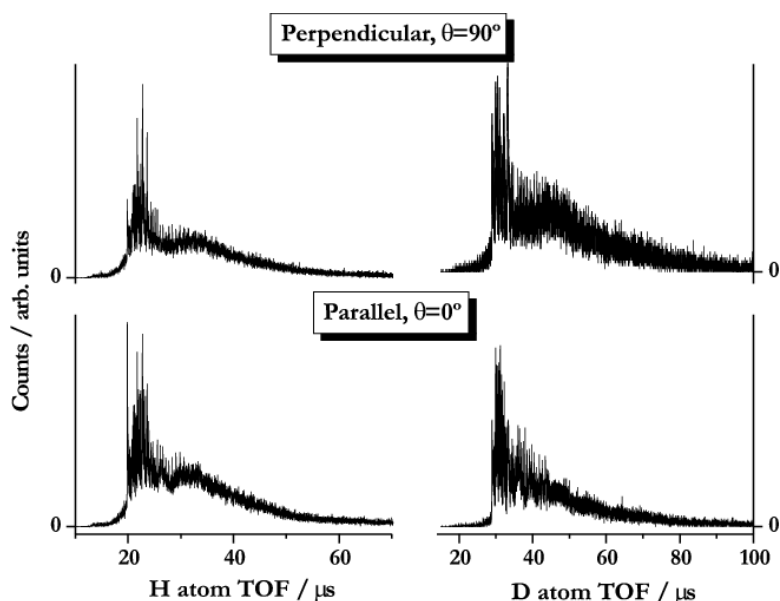
The apparatus re-design proceeded well during the refurbishment period, the necessary new parts were sourced and fabricated, and the enhanced apparatus rebuilt in early 2002. It worked from the outset. This was a major achievement on the part of both Rafay Qadiri and Dr Emma Feltham. Lyman- $\alpha$  generation occurs in a new, longer, frequency tripling cell, operated with phase matched Kr/Ar gas mixtures. The much improved efficiency and stability of this vacuum UV source gives much higher signal count rates and improved signal to noise ratio; one of the major operational difficulties with the previous apparatus has been eliminated. Experimental findings obtained during the period of the award are summarised below.



**Figure 1.** The rebuilt H (Rydberg) PTS apparatus

### Lyman- $\alpha$ Photodissociation of $\text{H}_2\text{S}$ and $\text{D}_2\text{S}$

The photochemistries of  $\text{H}_2\text{S}$  and  $\text{D}_2\text{S}$  at the respective H(D) Lyman- $\alpha$  wavelengths were reinvestigated with, for the first time, angular resolution of the H/D atom signal relative to the polarisation vector  $\epsilon$  of the photolysis radiation. The time-of-flight (TOF – fig. 2) and total kinetic energy release (TKER) profiles were found to consist of two distinct components.



**Figure 2** H/D atom TOF profiles for dissociation of  $\text{H}_2\text{S}$  (left hand column) and  $\text{D}_2\text{S}$  (right column) recorded under perpendicular (top row) and parallel (bottom row) polarizations of the photolysis radiation relative to the detection axis. In each case the parallel and perpendicular profiles are shown with the correct relative vertical scales.

One, which is highly structured, was assigned to two body dissociation to  $\text{H/D} + \text{SH/SD}(\text{A}^2\Sigma^+)$  fragments, with the latter formed in a broad range of internal quantum states. Assignment of these various levels led to

a refined value for the bond dissociation energy  $D_0(\text{D-SD}) \geq 31874 \pm 22 \text{ cm}^{-1}$ . The second component, which is broad and relatively structureless, was modelled in terms of two competing pathways; secondary predissociation of the nascent  $\text{SH/SD}(\text{A}^2\Sigma^+)$  partner fragments, and direct three body decay to  $2\text{H/D} + \text{S}(\text{D})$  atoms. Analysis of spectra recorded with  $\epsilon$  aligned at, respectively,  $0^\circ$ ,  $54.7^\circ$  and  $90^\circ$  to the detection axis allowed first determinations of the recoil anisotropy parameter  $\beta$  as a function of recoil energy.  $\beta$  was found to be positive for all recoil KEs, indicating that the H/D atoms prefer to recoil along axes parallel to  $\epsilon$ . We performed *ab initio* calculations of key regions of the various excited state PESs sampled in the fragmentation process, together with trajectory calculations on these surfaces; these successfully explained the absence of ground state  $\text{SH/SD}(\text{X}^2\Pi)$  products and provided much insight into the nature of the non-adiabatic transitions involved in the evolution from photo-excited molecule through to asymptotic products.<sup>2</sup>

### Vacuum ultraviolet photochemistry of methane, silane and germane

H Rydberg PTS was also applied to investigations of the photochemistry of jet-cooled  $\text{CH}_4$ ,  $\text{SiH}_4$  and  $\text{GeH}_4$  molecules following excitation at 121.6 nm.<sup>3</sup> Complementary *ab initio* calculations of selected portions of the PESs for the various components of the  $^1\text{T}_2$  and  $^3\text{T}_2$  excited states arising from the  $3s\text{a}_1 \leftarrow 1\text{t}_2$  electron promotion were performed also, for the case of  $\text{CH}_4$  only. The form of the H atom recoil velocity distribution arising in the 121.6 nm photolysis of  $\text{CH}_4$  was rationalised in terms of initial excitation to both the  $2^1\text{A}'$  and  $1^1\text{A}''$  excited states (Jahn-Teller components of the degenerate  $^1\text{T}_2$  state), followed by a range of decay mechanisms.  $\text{CH}_4(2^1\text{A}')$  molecules can decay adiabatically – via sequential extension of first one, then a second, C–H bond, with eventual formation of two H atoms and  $\text{CH}_2(\tilde{\text{a}}^1\text{A}_1)$  products – or after internal conversion (IC) to the ground state. The  $\text{H} + \text{CH}_3(\tilde{\text{X}})$  products resulting from the IC process display a recoil velocity distribution characterised by an anisotropy parameter  $\beta \sim +2$ , implying that the fragmentation involves irreversible extension of the C–H bond along which the transition dipole points at the instant of photon absorption. Fragmentation of  $\text{CH}_4(1^1\text{A}'')$  molecules to  $\text{H} + \text{CH}_3(\tilde{\text{X}})$  products proceeds via intersystem crossing (ISC) to the lowest  $^3\text{A}'$  PES. The measured recoil anisotropy parameter of these products ( $\beta \sim -0.45$ ) implies that this radiationless process also occurs on a timescale that is rapid compared to the parent rotational period. Both single H–C bond fission channels may yield  $\text{CH}_3(\tilde{\text{X}})$  products with such high levels of internal excitation that they are unstable with respect to further unimolecular decay; any H atoms that result from this secondary decay must contribute to the observed yield of slow H atoms with  $\beta \sim 0$ . All H atoms resulting from Lyman- $\alpha$  photolysis of both  $\text{SiH}_4$  and  $\text{GeH}_4$  have (low) KEs and little or no recoil anisotropy, compatible with their being formed via three body fragmentation to, primarily,  $\text{H} + \text{H} + \text{SiH}_2/\text{GeH}_2(\tilde{\text{X}}^1\text{A}_1)$  products. These findings, which have been reproduced in subsequent studies involving isotopic variants of  $\text{CH}_4$ ,<sup>9</sup> raise important questions about our understanding of the rates and probabilities of spin-changing radiationless processes in small polyatomic molecules like  $\text{CH}_4$  and demand further investigation at other, neighbouring, photolysis wavelengths.

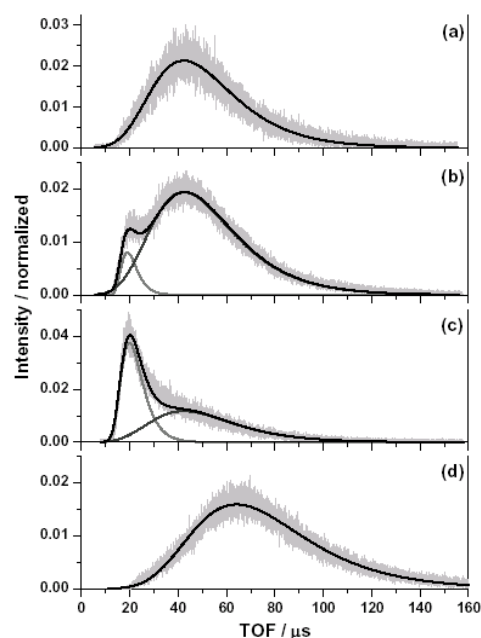
### UV photolysis of $\text{HN}_3$ molecules following excitation in the $\tilde{\text{A}}^1\text{A}'' \leftarrow \tilde{\text{X}}^1\text{A}'$ absorption band

The final phase of Phill Cook's Ph.D. research involved *ab initio* calculations of two-dimensional (2-D) cuts through the full 6-D PESs of the ground ( $\tilde{\text{X}}^1\text{A}'$ ) and first excited ( $\tilde{\text{A}}^1\text{A}''$ ) states of  $\text{HN}_3$ .<sup>4</sup> Specifically, we investigated the variation of the PESs with respect to simultaneous changes of the H–NNN and HN–NN bond lengths, and to changes of the H–NNN bond length and  $\angle\text{N–N–N}$  angle. These pairs of co-ordinates were chosen in the light of the deduced importance of each of these motions in interpreting the experimentally observed UV photochemistry of this molecule. In collaboration with Prof. R.N. Dixon, 2-D quantum mechanical wavepacket calculations of the photodissociation dynamics were carried out using each of these 2-D surfaces. The results offered strong support to our earlier interpretations<sup>8</sup> regarding the form of the vibrational energy disposal in the  $\text{N}_3(\tilde{\text{X}})$  products arising via H–NNN bond fission on the  $\tilde{\text{A}}$  state PES. The wavepacket calculations also allowed us to investigate factors influencing the relative branching into the competing H–NNN and HN–NN bond fission channels on the excited state PES, and to predict relative branching ratios for these two channels, as a function of excitation energy, in reasonable accord with the limited available experimental data.<sup>4</sup>

## UV photolysis of allene and propyne

The last experimental study prior to shutting down for the JIF refurbishment of our laboratories involved study of the fragmentation dynamics of allene and propyne (two structural isomers of  $C_3H_4$ ) following excitation at wavelengths in the range 203.3-213.3 nm.<sup>5</sup> The photofragmentation of both molecules had been investigated previously, at the ArF laser wavelength (193.3 nm). The dissociation of photoexcited allene molecules was deduced to proceed by IC to the ground state PES and subsequent unimolecular decay<sup>10</sup> but, in the case of propyne, the earlier studies<sup>11-14</sup> all deduced that the stronger, acetylenic, C–H bond broke in preference to the (weaker) methyl C–H bond – implying a markedly non-statistical, bond selective, fragmentation process. Contrary to these reports, we found the TKER spectra associated with the H atom product forming channel(s) in both molecules to be essentially identical, and to have a form that was reproduced well by an approximate statistical model that assumed population of all possible vibrational states of the partner fragment ( $H_2CCCH$ ) – implying that, at our excitation energies, both molecules underwent IC to, and isomerisation on, the ground state PES prior to fragmentation. The striking discrepancy between our findings, and the consensus view reached from the several earlier studies of propyne photolysis at 193.3 nm made it imperative that we investigated this further, and it was identified as a top priority post-refurbishment and re-assembly of the enhanced PTS apparatus. In the event, we found that the TKER spectra of the H atoms resulting from 193.3 nm photolysis of  $H_2CCCH_2$  and  $H_3CCCH$ , and of the H and D atoms from 193.3 nm photolysis of the isotopically labelled species  $D_3CCCH$  were all essentially identical,<sup>6</sup> reinforcing our earlier conclusion that fragmentation of both allene and propyne following near UV photoexcitation is preceded by IC to the ground state PES, and that the isomerisation rate of the resulting highly vibrationally excited  $C_3H_4^\ddagger$  molecules is faster than their rate of unimolecular decay.

The TOF and TKER spectra of the H and D atoms resulting from 121.6 nm photolysis of allene, propyne and propyne- $d_3$  were measured also (see fig. 3), and found to show significant differences.<sup>6</sup> These could be reconciled by assuming two competing pathways for forming H(D) atoms following photo-excitation of propyne. One, involving selective cleavage of the acetylenic  $H_3CCC-H$  bond, is assumed to occur from the excited electronic state prepared by photon absorption or from a recognizably ‘propyne-like’ state to which it couples efficiently. The other, which yields a slower distribution of H(D) atoms, is considered to arise via radiationless transfer to a lower electronic state, isomerisation and subsequent unimolecular decay. The TOF and TKER spectra of the H atoms resulting from 121.6 nm photolysis of allene are indistinguishable from those associated with this second, ‘statistical’ fragmentation channel in propyne.



**Figure 3.** H(D) atom TOF spectra resulting from photolysis of allene and propyne at 121.6 nm: (a) H atoms from  $CH_2CCH_2$ , (b) H from  $CH_3CCH$ , (c) H from  $^{13}CD_3CCH$ , and (d) D from  $^{13}CD_3CCH$ . The solid curves are fits to the data using model functions discussed in ref. 6.

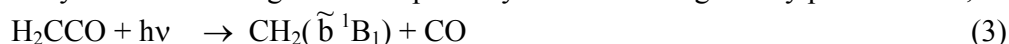
## UV photolysis of ketene

Ketene is another 16 valence electron molecule, like  $HN_3$ , allene and propyne and, as with the  $C_3H_4$  species, we recognised that the literature regarding  $CH_2CO$  photochemistry contained apparent contradictions. Most prior studies of ketene photochemistry have concentrated on C=C bond fission following excitation within the extensive near UV absorption system,<sup>15-17</sup> *i.e.*



Process (2) occurs via IC from the initially populated  $S_1$  state to the ground state. As such, it provides a textbook example of a fragmentation occurring on a PES with no exit channel barrier. Studies at, and just above, the energetic threshold have allowed precise determination of the dissociation energy ( $30116\text{ cm}^{-1}$ ) of ground state  $\text{CH}_2\text{CO}$  molecules to singlet products.<sup>15</sup> The electronic origin of the  $\tilde{a}^1A_1$  state of  $\text{CH}_2$  lies  $3147\text{ cm}^{-1}$  above that of the  $\tilde{X}^3B_1$  ground state. Thus process (1) is the lowest energy dissociation asymptote, but it is only accessible to those excited  $\text{CH}_2\text{CO}(S_1)$  molecules that undergo intersystem crossing, and dissociate on the first excited triplet ( $T_1$ ) PES. The  $T_1$  PES exhibits a small energy barrier ( $\sim 1280\text{ cm}^{-1}$ , measured relative to the zero point energies of the  $\text{CH}_2(\tilde{X}^3B_1) + \text{CO}$  fragments) to dissociation.<sup>15</sup> Process (1) thus has to be the sole dissociation channel following excitation at energies less than the threshold for process (2) but, once over this threshold, the singlet products rapidly become dominant – *e.g.* when ketene is photolysed at  $308\text{ nm}$  ( $\sim 2350\text{ cm}^{-1}$  above the threshold for channel (2)), the quantum yield of process (2) is at least  $10\times$  that of process (1).<sup>16,18,19</sup>

Our work focussed on ketene photochemistry following excitation at shorter wavelengths, in the banded  $S_2 - S_0$  absorption system. Other fragmentation pathways are now energetically possible also, including:



Most previous studies had focussed on excitation solely at  $193.3\text{ nm}$ . Analysis of IR emission from nascent CO fragments showed them to be rotationally and vibrationally excited,<sup>20,21</sup> the deduced vibrational state population distribution matches that predicted by a statistical model assuming IC to the ground state and dissociation via process (2).<sup>20</sup> Observations of HCCO fragments,<sup>22-25</sup> provide direct evidence for the participation of channel (4). Glass *et al.*<sup>26</sup> used resonance absorption methods to monitor relative H atom yields following  $193\text{ nm}$  photolysis of dilute ketene/Ar and ketene/ $\text{H}_2$  mixtures, together with the results of previous end-product analysis studies, to infer a dominant role for channel (1), (quantum yield,  $\Phi_1 \sim 0.63$ ), with  $\Phi_2 \sim 0.19$  and  $\Phi_4 \sim 0.11$ . Dissociation pathway (5), forming  $\text{C}_2\text{O}$  fragments (in their  $\tilde{b}^1\Sigma^+$  state) was also deduced to contribute  $\sim 7\%$  of the total fragment yield. Such branching ratios, if correct, appear incompatible with the view that dissociation of  $\text{CH}_2\text{CO}(S_2)$  molecules proceeds via radiationless transfer and subsequent unimolecular decay on the ground state PES. We therefore used our H (Rydberg) PTS method to investigate  $\text{CH}_2\text{CO}$  photolysis following excitation at a number of wavelengths in the range  $193.3 - 213.3\text{ nm}$ . Consistent with the previously deduced CO vibrational state population distributions,<sup>20,21</sup> our measured H atom translational energy distributions were all consistent with a dissociation mechanism involving one photon absorption to the  $S_2$  state, IC to high lying vibrational levels of the ground state and subsequent unimolecular decay to yield the observed H (+ HCCO) products.<sup>7</sup> H atoms resulting from secondary photolysis of H containing primary products (most probably  $\text{CH}_2$  radicals) were also evident in the measured spectra, especially at high photolysis laser pulse energies.

This work also served to inspire colleague Prof. G.G. Balint-Kurti (together with Ph.D. student John Cole) to develop a new, quantum mechanical,  $J$  conserving, Rice-Ramsperger-Kassel-Marcus (RRKM) treatment (the Statistical Adiabatic Product Distribution (SAPD) method) to describe not just the rates but also the product state distributions arising in photo-initiated unimolecular dissociations.<sup>27</sup> Accurate, quadratic configuration interaction, intrinsic reaction coordinates have been computed for both the  $S_0$  and  $T_1$  PESs of  $\text{CH}_2\text{CO}$ , and quantum mechanical SAPD calculations performed using both surfaces. Unsurprisingly, the calculations employing the  $S_0$  potential provide the better replication of the measured TKER spectra and CO product quantum state distributions. Different aspects of the SAPD model, such as the inclusion of quantum mechanical tunnelling, the attractiveness of the long-range inter-fragment potential and the assumed adiabaticity of the fragmentation, were varied in order to shed light on the nature of the dissociation process and the possible origins of remaining differences between the model calculations and the experimental results. Agreement between the model predictions and the measured TKER spectra for the H atom dissociation channel can be greatly improved if the contribution of lower fragment relative orbital angular momenta is increased over that required by the use of a purely statistical model. This finding is equivalent to the conclusion that the dissociation is not entirely statistical, but that the dynamics of the break-up process

plays some role. In particular, the initial geometry of the parent molecule may restrict the body-fixed angles into which the final products can scatter and, through this, may restrict the relative orbital angular momenta to be on average smaller than that predicted by a purely statistical theory.<sup>7</sup>

## Research Impact, Explanation of Expenditure and Further Research and Dissemination Activities

Work supported by this award has been described in a number of presentations at international conferences (e.g. Chemical Society of Thailand Annual Conference, Bangkok, 12/00; Optical Society of America Annual Meeting/ILS-XVII, Long Beach, California, 10/01; 223<sup>rd</sup> ACS National Meeting, Orlando, Florida, 4/02; 225<sup>th</sup> ACS National Meeting, New Orleans, Miss., 3/03; and Conference on Molecular Energy Transfer, COMET XVIII, El Escorial, Spain, 6/03), and at various smaller national meetings. New standards have been defined for each of the systems under study – in terms of the resolution of product energy states, the level and detail of the interpretation and, in the cases of allene, propyne and ketene, by resolving significant discrepancies and/or misconceptions in the existing scientific literature. The complementary theoretical developments inspired by the experimental studies of ketene fragmentation, and the recognition of constraints imposed by angular momentum conservation, is likely to impact on future discussions of what constitutes ‘statistical’ energy disposal in unimolecular decay processes. These levels of achievement would not have been possible without the financial support of several agencies – EPSRC, the Leverhulme Trust and an EU TMR programme (IMAGINE), nor would the work have been anything like so complete without the substantial input offered by other members of the Molecular Science Group at Bristol (notably Dr A.J. Orr-Ewing and Profs. G.G. Balint-Kurti and R.N. Dixon). Expenditure was very much along the lines originally planned. The hydride radical photochemistry studies originally proposed in this application are now underway, in the hands of new Ph.D. students Mike Nix and Brid Cronin, courtesy of EPSRC Portfolio award (GR/S71750) and additional EU funding through the TMR network PICNIC (coordinated by Dr. B.J. Whitaker (Leeds)).

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