Correlated Photochemistry: The Legacy of Johann Christian Doppler

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I. Introduction

Fields of scientific endeavor, like sonatas in music, are divided into movements. Most often we experience the steady progress of an *allegro assai*, but occasionally this tempo is punctuated by the contemplative creativity of an *adagio serioso* or even the excitement of a *presto furioso*. To physical chemists, the field of photochemistry had its first real *presto* when Norrish and Porter developed flash photolysis/transient absorption spectroscopy in the 1950s.[1] In observing the internal energy states of photofragments, they demonstrated the first technique that provided information about the *dynamics* of a photodissociative event. Chemists could finally learn how individual parts of a molecule respond to the rupture of a specific bond. After a brief return to *allegro assai*, the tempo of the photochemistry movement accelerated *con fuoco* with the introduction of lasers in the 1960s and, in particular, the development of laser-induced fluorescence by Zare and his co-workers.[2] This technique provided seemingly infinite resolution, both in the excitation of molecules by the absorption of monochromatic photons and in the detection of individual states of the products. Electronic, vibrational, rotational, and even hyperfine levels became easily accessible for examination. With the development of laser sources of yet higher resolution, it has now become possible to determine not only the distribution over all internal energy levels in the photofragment but also the distribution of recoil velocities for a photofragment in a selected internal energy level. The basic physics that provides us with knowledge of the velocity of a state-selected photofragment was worked out by Johann Christian Doppler in 1845, and our use of the effect that bears his name makes it possible for the first time to perform correlated photochemistry.

Correlated photochemistry concerns the relationship between two or more measurable properties in a photodissociative event. It is convenient for discussion purposes to separate these properties into scalar quantities, which have simply a magnitude, and vector quantities, which have both a magnitude and a direction. Examples of scalar quantities include such observables as the quantum yield of dissociation, the en-

ergy in rotation or vibration of a particular fragment, or the total energy in one of, say, two photofragments. Vector quantities include such observables as the recoil velocity (both magnitude and direction) between two photofragments, the angular momentum associated with rotation of one of the fragments, and the direction and strength of the transition dipole moment responsible for absorption by the parent molecule. This Account will attempt to demonstrate how correlations between either scalar quantities or vector quantities can provide substantially more information about the photodissociative event than knowledge of the quantities in isolation from one another, in other words, that the whole is more than the sum of its parts. Although the literature is currently exploding with examples of these correlations, the work described below will be nearly all from my own research program. The reader interested in a wider view of vector correlations can find a summary in a recent review.[3] Since much of our knowledge of these correlations comes from measurements involving the Doppler effect, it is well to begin with a review of the basic ideas developed by this 19th century physicist.

II. Johann Doppler and Scalar Correlations

Johann Christian Doppler was born in Salzburg in 1803. The son of a stone mason, he was forced by fragile health to forgo his father's profession and pursue other alternatives. No doubt, his choices first of business and then of an academic career were influenced by his mathematical abilities. But like many scientists of my own generation, Doppler was discouraged by the job market he encountered after graduating from Vienna Polytechnic Institute in 1825. He was almost on the verge of emigrating to America when he finally was offered a post at a secondary school in Prague. He progressed to the Prague State Technical Academy and in 1850 became the Professor of Physics at the Royal Imperial University in Vienna, just after having performed his most famous experiment. The effect that bears his name is familiar to all: the frequency of a sound wave heard by an observer depends on the relative speed between the observer and the source of the sound. It was actually Armand Fizeau in 1848 who pointed out that the same effect occurred for light waves. Specifically, the frequency of light absorbed by a moving object is shifted by an amount that depends on the relative velocity between the light source and the object: $\nu_{abs} = \nu_0[1 - (v/c)]$, where ν_0 is the frequency that would be absorbed in the absence of relative motion, v is the relative velocity, and c is the

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speed of light. Thus, if a molecule to be probed by laser–induced fluorescence is moving toward the laser, it will absorb at a slightly lower frequency than if it is moving away from the laser. The distribution of absorption frequencies is thus directly related to the distribution of molecular speeds.

Most chemists first encounter the Doppler effect as the cause for broadening of spectral lines at low pressures. If molecules have a Maxwellian distribution of speeds, their spectral line shape will be Gaussian with a half-width proportional to the square root of the temperature. It is less well-known that an ensemble of molecules having velocities isotropic in space but characterized by a single speed v exhibits a Doppler profile of equal absorption intensity throughout the line but with sharp edges at frequencies $\nu = \nu_0[1 \pm (v/c)]$. For an arbitrary distribution of speeds, but still for an isotropic distribution in space, the speed distribution $P(v)$ is simply proportional to the derivative of the Doppler profile at the frequency ν corresponding to the velocity v.[3] As we will see below, the relationship is less simple if the velocity distribution is not isotropic or if there are angular relationships between the velocity vector and the angular momentum vector, but even in these cases, multiple measurements of the Doppler profile using different detection geometries or different spectral transitions can lead unambiguously to the distribution of speeds.

Once we learn the speed distribution of a state-selected photofragment, then we automatically know something about the energy distribution of the sibling fragment, since conservation of energy requires that the energy of the photon plus the energy of the parent molecule be equal to the sum of the dissociation energy, the recoil energy, and the internal energies of the two fragments:

$$E_{h\nu} + E_{parent} = E_d + E_r + E_1 + E_2 \qquad (1)$$

In this manner, the determination of the speed distribution for a state-selected photofragment makes possible a coincidence-like measurement of the energy state of the other fragment. In terms of our discussion above, this is a scalar–scalar correlation between the energies in sibling photofragments.

Consider the example of photodissociation of OCS at 222 nm,[5,6] yielding either $CO + S(^3P)$ or $CO + S(^1D)$. For the former channel, nearly 20 000 cm^{-1} of energy is available for excitation of the CO internal degrees of freedom and the S–CO recoil velocity, whereas in the latter channel, only about 10 000 cm^{-1} is available. The observed rotational distribution of the CO(v=0) was measured by tunable vacuum ultraviolet laser induced fluorescence and found to be unusual in two respects. First, the rotational distribution is inverted; there is abundant population between $J = 50$ and $J = 69$, but little or none at lower rotational levels. Apparently, the OCS, which is linear in its ground electronic state, is subjected to a substantial bending force as it breaks apart. The second unusual aspect of the rotational distribution is that it is bimodal, with two peaks at $J = 54$ and $J = 65$. At first it was tempting to identify

these two peaks with the two channels;[5] the peak at $J = 65$ might be due to those CO molecules produced in coincidence with $S(^3P)$, while the peak at $J = 54$ could correspond to the CO molecules produced in coincidence with $S(^1D)$. Johann Doppler rescued us from this false identification.[6] The $S(^3P)$ channel has much more energy available, and the internal energy for CO with $J = 65$ is not much more than that for CO with $J = 54$. If our original speculation were true, then the CO in $J = 65$, supposedly from the $S(^3P)$ channel, should have an appreciably higher recoil velocity than that of $J = 54$, from the $S(^1D)$ channel. In fact, the Doppler profile for CO(J=65) was actually *narrower* than that for CO(J=54); both widths corresponded exactly to the values calculated on the basis of a single $CO + S(^1D)$ channel. The Doppler widths thus helped to establish a scalar–scalar correlation between the internal energy of the CO fragment and that of the S fragment. Of course the cause for the bimodal CO rotational distribution remains a question, one that we will address later in section IV. Before doing that, however, it is instructive to see how the Doppler profiles can also tell us something about vector correlations.

III. The Anisotropy of Photofragment Recoil

If Norrish and Porter provided photochemistry with a *presto* of experimental activity, then it was Zare and Herschbach who provided the field with the *adagio serioso* of contemplative inspiration. In order to understand their seminal contribution, it is useful to consider the various frames of reference important to molecular photodissociation. Consider an experiment in which an isolated molecule is excited with linearly polarized light and subsequently dissociates to yield two fragments recoiling from one another. The frame of reference most easily understood is the laboratory frame, defined for example by the polarization direction of the light used for molecular excitation. This direction is that of the electric field of the light, $\hat{E}$. A second important frame of reference is that of the parent molecule. It is usually defined by some symmetry element, such as a reflection plane or rotation axis, but for our purposes the important symmetry element will be the direction of the transition dipole moment, μ. For an allowed electronic transition from a symmetric ground state, this moment has the same symmetry as the electronic symmetry of the excited molecular orbital. A final frame of reference of importance for our discussion is that of the fragments. This frame is most easily defined by such elements as the direction of the recoil velocity, v, or the direction of the angular momentum, J, of one of the fragments. Although these vectors define the frame of reference of the fragments, they are also usually distributed in some set way in the reference frame of the parent molecule; for example, the vector v for the fragments is often along the direction of a breaking bond in the parent.

What Zare and Herschbach did was to relate these three frames of reference. In retrospect, the relationship seems simple to understand. At the start of the experiment, the molecular frames are distributed randomly in the laboratory frame. However, immediately after the absorption of the photon, the molecular frames of the *excited* molecules will have a definite laboratory alignment, since the strength of absorption is proportional to the product $|\mu \cdot \hat{E}|^2$. Thus, the excited molecules

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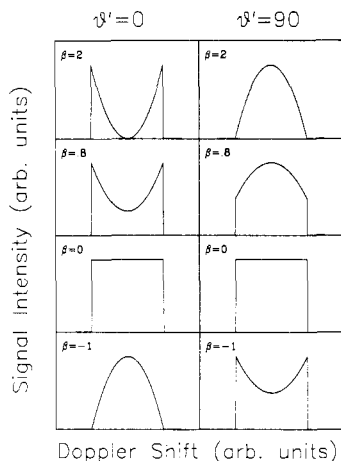
Figure 1. Examples of Doppler profiles predicted for a photofragment with a single speed and with various degrees of spatial anisotropy, characterized by the parameter β in the formula $I(\cos \chi) = [1 + \beta P_2(\cos \vartheta')P_2(\cos \chi)]$, where χ is the angle between the recoil velocity and the probe direction and ϑ' is the angle between the electric vector $\hat{\mathbf{E}}$ and the probe direction $\hat{\mathbf{k}}$. The value of $\beta = 0$ indicates an isotropic distribution, while $\beta = 2$ indicates that the recoil velocity $\mathbf{v}$ is parallel to the transition dipole moment μ, and $\beta = -1$ indicates that $\mathbf{v}$ and μ are perpendicular. The left column is for $\vartheta' = 0°$ (e.g., horizontal polarization of $\hat{\mathbf{E}}$ and horizontal probe direction $\hat{\mathbf{k}}$), while the right column is for $\vartheta' = 90°$ (e.g., vertical polarization and horizontal probe direction).

will have a distribution of alignments proportional to $\cos^2 \theta$, where θ is the angle between the molecular transition dipole and the laboratory electric vector. If these molecules dissociate very rapidly compared to rotational time scales, then the recoil velocity $\mathbf{v}$ of the fragments, which usually has a fixed relationship to the transition dipole μ, will also be aligned in the laboratory frame. Experiments first detected this anisotropy of fragment recoil by the uneven etching of a tellurium coating on a hemisphere bulb following dissociation of low-pressure Br_2 or I_2 with polarized light.[7,8] A more quantitative method used a mass spectrometer to measure the flux of fragments as a function of the angle between the electric vector and the flight direction.[9,10] But Zare and Herschbach also predicted that the anisotropy of recoil velocities would affect the Doppler profile of emission and absorption lines.[7]

To see why, consider an example in which a linear molecule with a transition moment along the breaking bond is dissociated by linearly polarized light. If the dissociation is rapid enough, then we would expect the photofragments to be ejected so that their recoil velocity is preferentially parallel to $\hat{\mathbf{E}}$. Suppose further that the photofragments are probed by absorption (or laser-induced fluorescence) using light propagating either parallel or perpendicular to $\hat{\mathbf{E}}$. For the parallel case, most photofragments will be moving either toward or away from the source of probe light with very few moving perpendicular to the probe direction; the absorption will thus be strong in the wings of the transition and weak at the center frequency, giving rise to a split Doppler profile. For the perpendicular case,

however, most molecules will be moving at right angles to the probe direction and will absorb at line center, with few absorbing in the wings. The quantitative Doppler profiles for these two cases are depicted in the top left and right panels of Figure 1, respectively. In the general case, the Doppler profile is given as $I(\cos \chi) = [1 + \beta P_2(\cos \vartheta')P_2(\cos \chi)]$, where ϑ' is the angle between $\hat{\mathbf{E}}$ and the probe direction $\hat{\mathbf{k}}$, χ is the angle between $\mathbf{v}$ and $\hat{\mathbf{k}}$, P_2 is the second Legendre polynomial, and $-1 \leq \beta \leq 2$ is a parameter that characterizes the anisotropy of the spatial distribution of velocity vectors, with $\beta = 0$ being a completely isotropic distribution.[7,11] Figure 1 shows Doppler profiles calculated for a photofragment with a single speed, for $\vartheta' = 0°$ or $90°$, and for four different values of β, ranging from $\beta = 2$ for a "parallel" transition (μ and $\mathbf{v}$ parallel) to $\beta = -1$ for a "perpendicular" transition.

Actual data for the 222-nm photodissociation of OCS, referred to in section II, is shown in Figure 2. Let us concentrate first on the data for the Q(58) line in horizontal ($\vartheta' = 0°$) and vertical ($\vartheta' = 90°$) polarization (third row, first two columns). Qualitatively, by comparison to Figure 1, it would appear that the photodissociation is characterized by a value of β somewhere between 0.8 and 0.0; i.e., a predominantly parallel transition. Quantitatively, however, there is a clear discrepancy between the predictions of Figure 1 and the experimental profiles of Figure 2. The value β characterizes the shape of the anisotropic distribution. Although the projection of this distribution onto the velocity axis may change with viewing angle ϑ', the three-dimensional shape of the object is not changed by viewing it from another angle; i.e., the measured value of β should not change as we change from $\vartheta' = 0°$ to $\vartheta' = 90°$. Yet the horizontal geometry seems to indicate a value of $\beta \approx 0.8$, while the vertical geometry indicates a value of $\beta \approx 0$. This discrepancy was the first indication to our group that the previous theory, while qualitatively correct, was quantitatively wrong. Figure 2 shows that the situation is actually much worse, since there is nothing in the previous theory to indicate that measurements on different transitions, say Q(58) compared to P(58), should give different Doppler profiles. To see what is wrong with the previous theory, we must consider what happens when the vectors $\mathbf{v}$ and $\mathbf{J}$ are correlated.

IV. The v–J Correlation

It should come as no surprise that the vectors $\mathbf{v}$ and $\mathbf{J}$, both defined in the frame of the photofragments, might have an angular correlation. Consider, for example, the dissociation of a bent triatomic molecule from its rotationless state. If all the forces act in the plane of the molecule, then both the rotation of the diatomic fragment and the relative recoil will be in that plane, so that the rotational angular momentum vector, $\mathbf{J}$, will be perpendicular to the plane and also to $\mathbf{v}$. Although Case, McClelland, and Herschbach[12] briefly mentioned that such a correlation might affect the Doppler profile, it was the discovery, nearly simultaneously in four groups,[13–16] of discrepancies such as

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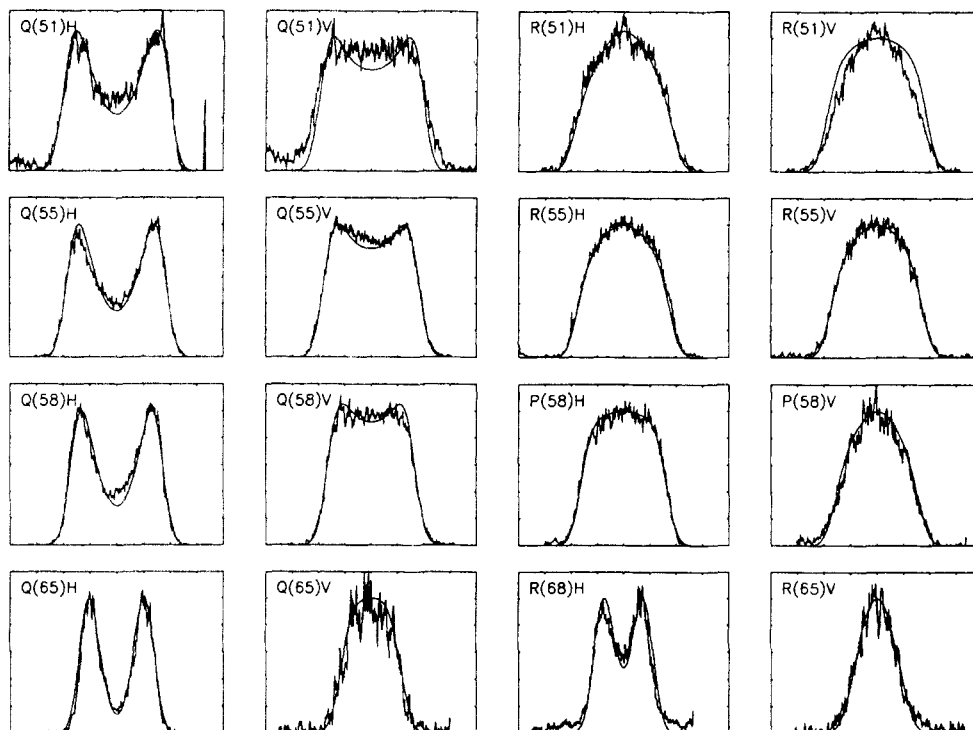
Figure 2. Doppler profiles of representative CO(J) lines taken on different transitions and with different geometrical arrangements. Q(J), P(J), and R(J) represent the different branches; H represents horizontal geometry ($\vartheta' = 0°$), while V represents vertical geometry ($\vartheta' = 90°$). The smooth lines are the predicted profiles based on the model described in the text. The scale on the abscissa of each plot is laser detuning from −0.5 to +0.5 cm^{-1}. Reprinted with permission from ref 6. Copyright 1988 American Institute of Physics.
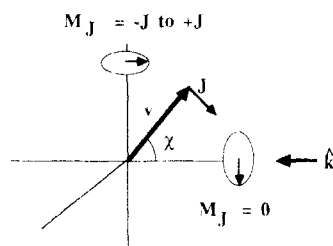
Figure 3. M_J distribution as a function of Doppler shift, cos χ, when v and J are perpendicular. Reprinted with permission from ref 19. Copyright 1987 American Chemical Society.

those between the calculations of Figure 1 and the data of Figure 2, that made this field accelerate once again to a *presto*. A complete and detailed theory for the effect is now available,[13,17,18] but a simple physical rationalization can be obtained from Figure 3.[19]

Consider a system, such as the triatomic dissociation mentioned in the preceding paragraph, in which the velocity and angular momentum vectors are constrained by the dissociation to be perpendicular to one another. Further assume for simplicity that the velocity vectors are distributed isotropically in space, so that the previous theory, which ignored correlations between v and J, would predict a "flat-topped" Doppler profile ($\beta = 0$, Figure 1). If v and J are constrained to be perpendicular to one another, it is easy to show that the

Doppler profile will actually have a modulation; it will no longer be flat-topped. The strength of the absorption by the fragment will depend on its M_J distribution, since diatoms with different orientations will interact differently with the polarized light of the probe laser. Consider the M_J distribution as a function of Doppler shift when v ⊥ J. For simplicity, we take the z axis in Figure 3 to be along the probe direction $\hat{k}$. In the wings of the profile, when v is along the probe direction $\hat{k}$, then the projection of J onto the axis $\hat{k}$ (=z) will give only one value, $M_J = 0$. On the other hand, in the center of the Doppler profile where v is perpendicular to $\hat{k}$, the projection of J onto $\hat{k}$ will have the entire range of values, $M_J = J$ to $M_J = -J$. Since the M_J distribution changes with Doppler shift, so will the strength of absorption. Therefore, the Doppler profile must be modulated; i.e., it contains information about the angular correlation of v with J. A detailed examination of the fragment absorption shows that for v ⊥ J, Q-branch transitions (with $\Delta J = 0$) should have a dip in the center of the Doppler profile, while R- or P-branch transitions (with $\Delta J = \pm 1$) should have a peak. For v ∥ J the situation is reversed. [The physical basis for this difference between Q-branch and R- and P-branch transitions is that for the former transitions the transition dipole of the diatomic molecule is parallel to J (in the classical limit), while in the latter it is perpendicular.]

The above example assumed an isotropic distribution of v and showed that the Doppler profiles for fragments should reflect whether their rotation vector is perpendicular or parallel to their velocity vector. When the distribution is not isotropic, the Doppler profile will carry information both about the anisotropy of v in the laboratory frame and about the correlation between v and J. The data of Figure 2 can be understood if it is

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assumed that **v** and **J** are constrained to be perpendicular in this dissociation and that the anisotropy, characterized by the value of β, varies with the rotational level probed. The angular constraint on **v** and **J** is reasonable since (1) we know that the OCS bends on dissociation (giving rise to the large amount of CO rotational excitation), (2) the OCS in our experiment is nearly all prepared in the rotationless level, and (3) we have already seen that the dissociation of a rotationless triatomic molecule should give **v** ⊥ **J**, assuming all forces to operate in the molecular plane. But why should the value of β depend so strongly on the rotational state probed? The answer to this question turns out to be quite interesting, since it also provides the reason why the rotational distribution has two maxima.

The transition that excites the OCS molecule at the wavelength used in our experiment is assigned as $^1\Sigma \rightarrow {}^1\Delta$.[20] Although this transition would normally be forbidden, it might become allowed if the upper state were actually bent rather than linear. When a $^1\Delta$ state is deformed by bending, according to the Renner–Teller effect, it splits into two states of A' and A'' symmetry.[21] For the former state, the transition moment μ lies in the plane of the molecule (let us suppose that it is parallel to the breaking bond), while in the latter state, it lies perpendicular to the plane. If we assume that the two peaks in the rotational distribution come from dissociation on these two different surfaces, it might be reasonable to infer that β will change from a value near 2 for levels produced by dissociation on the former surface to a value near −1 for levels produced by dissociation on the latter surface. In fact, we find that the value of β decreases smoothly with rotational level and that the Doppler profiles observed are in excellent agreement with calculations (smooth solid lines in Figure 2) based on the simple assumption that higher rotational levels come from the A' surface, that lower ones come from the A'' surface, and that the fraction of molecules in a particular J level coming from the A' surface falls smoothly with J.

Let us step back for a moment and summarize what we have learned. We have seen that the polarized light field aligns the transition dipole moment μ in the laboratory frame. If dissociation is rapid compared to parent rotation, this alignment results in an anisotropy of recoil velocity vectors in the laboratory frame which affects the Doppler profile. Furthermore, the act of dissociation imparts to the fragments both recoil velocity and rotational angular momentum. The vectors describing these motions, **v** and **J**, have an angular correlation which also modulates the Doppler profile. In addition to modulating the Doppler profile differently, these two effects, the anisotropy and the **v**–**J** correlation, have an important physical distinction. The anisotropy tends to be diminished if the parent molecule rotates substantially between the absorption and the dissociation, but the **v**–**J** correlation is not affected by parent rotation, since it is not made until the moment that the parent molecule falls apart. This difference is illustrated nicely by the example of glyoxal photodissociation.

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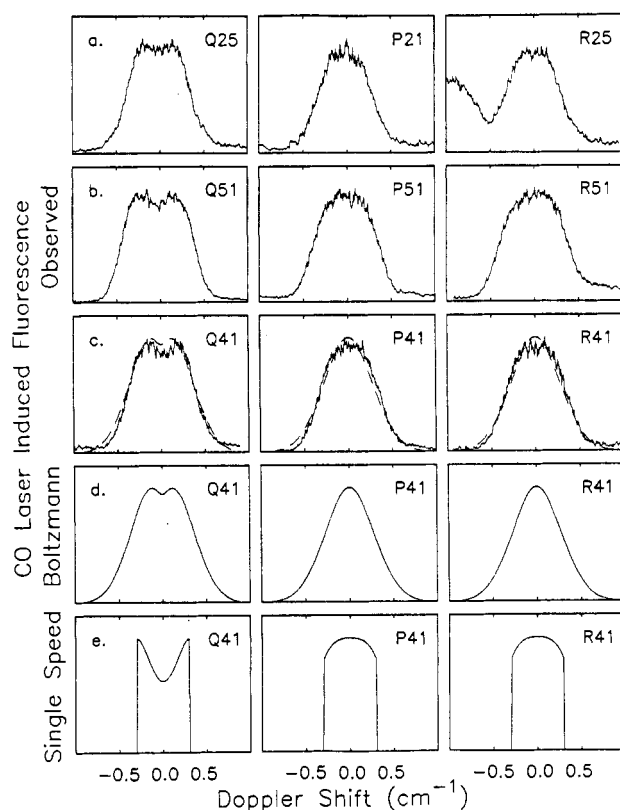

Figure 4. Calculated and experimental Doppler profiles for CO produced in the photodissociation of glyoxal. Rows a–c: representative experimental data for Q(J) (left-hand side), P(J) (center), and R(J) (right-hand side) transitions. The distinctive line shapes of the Q vs P and R lines persist throughout the complete Doppler profile data set spanning J = 20–59. Rows d and e: calculated Doppler profiles assuming a **v** perpendicular to **J** correlation. Row e is for a single CO recoil velocity, while row d is for a Boltzmann distribution of recoil speeds. The dashed line in row c is a superposition onto the data of the Doppler profiles shown in row d. Reprinted with permission from ref 22. Copyright 1987 American Institute of Physics.

When excited to low-lying vibrational levels of S_1, the trans-planar molecule glyoxal dissociates to give CO and several possible sibling fragments:

$$CHOCHO + h\nu \rightarrow H_2CO + CO \qquad (2)$$

$$\rightarrow H_2 + 2CO \qquad (3)$$

$$\rightarrow HCOH + CO \qquad (4)$$
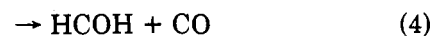
Our group has investigated this dissociation by probing the CO fragment with laser-induced fluorescence.[22] Because the dissociation has a lifetime on the order of 1 μs, it is expected that any anisotropy in fragment recoil will be greatly diminished. Isotropic fragmentation, in the absence of any **v**–**J** correlation, would result in a flat-topped Doppler profile for each recoil velocity. As described above, in the presence of a **v**–**J** correlation, Q-branch transitions acquire a different shape than P- or R-branch transitions. If the dissociation takes place with considerable torsional motion about the C–C bond, then we might expect **v** to be parallel to **J**, whereas, if the dissociation takes place entirely in a plane, then the CO should both rotate and translate in the plane so that **v** would be perpendicular to **J**. Row e in Figure 4 shows the expected Doppler profiles for CO, assuming that the

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CO has a single speed and that **v** and **J** are perpendicular to one another; the Q-branch lines are predicted to have a dip in the center, whereas the P- and R-branch lines have a peak. Of course, with three possible dissociation channels and with differing internal energies in the sibling fragments, the CO will have a wide distribution of speeds. Row d of Figure 4 shows that even after averaging over a 5600 K thermal speed distribution for the CO, the difference in Q vs P- and R-branch line shapes persists. The observed shapes of the Q, P, and R lines are illustrated in rows a–c of Figure 4 and are typical of those observed throughout the complete Doppler profile data set spanning $J = 20$–59. The fact that all Q-branch lines have a dip in the center, whereas the P- and R- branch lines do not, is strong evidence that **v** and **J** are constrained to be perpendicular to one another, in accord with the planar dissociation mechanism. It is interesting to note that the transition state precicted from ab initio calculations is also planar.[23]

V. Conclusions

Correlated photochemistry is settling back again into the pace of an *allegro assai*, but it is certainly yielding a higher level of enjoyment and information than ever before. Scalar correlations, unveiled through use of Doppler spectroscopy, have provided information for the first time about the internal energy of a sibling fragment born in coincidence with a state-selected product. The Doppler profiles, and particularly their variation with experimental geometry and fragment transition, have provided exciting new information about vector correlations. The time scale of dissociation relative to the parent rotational period can be inferred from the recoil anisotropy, and the direction of the transition dipole in the parent compound can be assigned. The correlation between the recoil velocity and fragment angular momentum vectors affords even more detail about the symmetry of the excited state and provides as well important information about the geometry of transition state reached just before dissociation. This information is not lost even if the parent molecule has a dissociation lifetime that is long compared to its rotational period.

Where will correlated photochemistry lead, and where should we look for the first notes of the next *presto*?

Certainly the techniques described in this Account (and some other techniques which there was not room to include) will be applied to a large number of dissociative systems, providing, hopefully, new insight into the dynamics of separation into fragments. As experimentalists develop lasers of higher resolution as well as methods for better preparation of the parent molecule, we can expect that the amount of detail uncovered from the Doppler profiles will increase dramatically. Nonetheless, since Doppler profiles are essentially a one-dimensional projection of the velocity distribution, they contain substantial averaging over the details we wish to uncover. Three-dimensional imaging techniques, just now under development,[24-27] will help to retrieve these details. It may be possible as well to find techniques for determining more complicated vector correlations, such as the relationship between angular momentum vectors of two different fragments. Finally, despite the fact that most of the vector correlations measured thus far concern *alignment*, where the directional properties have inversion symmetry, it is clear that even more information can be gained from *orientational* properties, measured by using circularly polarized light for both the dissociation and probe steps. Indeed, investigations along this line have already begun.[28,29] With continued ingenuity and further advances in instrumentation, the symphony of correlated photochemistry may well continue through several more movements before coming to its *finale*.

Registry No. Glyoxal, 107-22-2.

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