

Photodissociation dynamics of formaldehyde: H_2 (v, J) vector correlations

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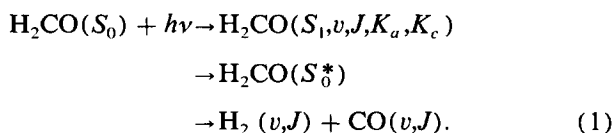
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Several bipolar moments of the H_2 (v, J) correlated angular momentum and velocity distribution produced from the photodissociation of formaldehyde near the threshold for dissociation have been measured by analysis of Doppler-resolved LIF line shapes. It is determined that the fragment H_2 ($\mathbf{v} \cdot \mathbf{J}$) correlation is not at the limit of $\mathbf{v} \perp \mathbf{J}$, but is closer to the limit of $\mathbf{v} \parallel \mathbf{J}$ than to $\mathbf{v} \perp \mathbf{J}$. The rotation of the excited H_2CO during the 10^{-7} – 10^{-8} s before dissociation does not completely wash out the lab-frame vector correlations. Anisotropy parameters as large as 0.85 and as small as -0.41 have been measured; these are outside the limits imposed by classical models of parent rotation. A quantum mechanical model for parent rotation is introduced that accounts for the large magnitude of the measured anisotropy parameters. Photolysis on the $^1R_0(0)$ line of the 4^3 band produces fragments with $\beta < 0$ while photolysis on the same rotational transition of the 2^14^1 band produces fragments with $\beta > 0$. It is not known if the different anisotropies are caused by differences in the parent transition dipole moment or by differences in the dissociation dynamics. The simple impulsive model that reproduces the fragment rotational distributions and product quantum-state correlations does not adequately describe the measured H_2 (v, J) vector correlations.

I. INTRODUCTION

Formaldehyde is an excellent molecule for the study of photofragmentation for a variety of reasons.¹ Its well resolved $S_1 \leftarrow S_0$ spectrum allows excitation to single rovibronic levels and the reaction dynamics can be unraveled in great detail as all photodissociation products can be probed.^{2–7} This system is also theoretically tractable with state-of-the-art *ab initio* techniques.^{8–12}

The mechanism for molecular dissociation is well known:¹



The electronically excited H_2CO internally converts to highly excited vibrational levels of the ground electronic state, where it dissociates over a steep barrier. Past studies of the photofragmentation have concentrated on the energy disposal in the products. These include measurements of the CO vibrational distribution,² the $\text{CO}(v, J)$ distribution by laser-induced fluorescence (LIF),³ the *ortho* H_2 (v, J) distribution by coherent anti-Stokes Raman spectroscopy (CARS),^{4,5} and the translational energy distribution by time-of-flight mass spectrometry.¹³ For photolysis energies near the barrier to dissociation, the CO product is highly rotationally excited with little vibrational energy (88% in $v = 0$).² The H_2 vibrational distribution^{4,5} peaks at $v = 1$ and the rotational distribution is approximately Boltzmann-like with T_{rot} decreasing as the vibrational state increases.^{5,7} Most of the available energy released (65%) appears as relative translational energy.

Past experiments have measured the scalar properties of formaldehyde photodissociation. Recently, it has become possible to determine vector correlations from the analysis of fragment LIF Doppler profiles.^{14–17} The vectors involved are the photolysis laser polarization ϵ_p , the transition dipole moment of the parent molecule μ , the velocity of the fragment $\mathbf{v}$, and the angular momentum of the fragment $\mathbf{J}$. The excitation laser preferentially excites parent molecules whose transition dipole moments are along the polarization axis of the laser. Although the parent dissociates on a time scale long compared to its rotational period, the anisotropy of the rotational state of the excited parent is carried over to the fragment's translational recoil direction and angular momentum vector. This results in $\langle \mu \cdot \mathbf{v} \rangle$, $\langle \mu \cdot \mathbf{J} \rangle$, and $\langle \mu \cdot \mathbf{v} \cdot \mathbf{J} \rangle$ correlations. In addition, the repulsive force of the dissociation can result in a $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation, which unlike the other correlations, is not smeared out by parent rotation. A full set of these correlations exists for each fragment, H_2 and CO. The magnitudes of these vector correlations are sensitive to the photofragmentation dynamics and should provide good tests of dynamical models and potential surface shapes.

This work is a continuation of the most recent experiments,^{6,7} where *ortho* and *para* H_2 rotational distributions and alignments were measured from the photodissociation of formaldehyde in a molecular jet under collisionless conditions using Doppler-resolved vacuum ultraviolet (VUV) LIF spectroscopy. It was found that the rotational distributions of *ortho* and *para* H_2 from H_2CO photolysis near the barrier to dissociation are Boltzmann-like ($J_{\text{peak}} \approx 3\text{--}4$) and of nearly identical shape.⁷ In addition, a product quantum state correlation was observed: higher vibrational states of H_2 are correlated with lower rotational states of CO.^{6,7}

This paper reports the H_2 (v, J) vector correlation measurements obtained from the Doppler-resolved LIF line shapes. Dixon's¹⁴ expansion of the correlated angular momentum and velocity distribution in terms of the expectation

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values of bipolar harmonics is used for the data analysis described in Sec. II. In Sec. III, Dixon's line shape analysis is shown to agree well with Hall *et al.*'s^{16,17} density matrix quantum approach for fragments with $J = 1$. Section III also discusses the vector correlation results and compares them to the results of the simple impulsive model that previously has had success describing the H_2 and CO rotational distributions and product quantum state correlations.⁷

II. ANALYSIS AND RESULTS

The experimental details have previously been described.⁷ Formaldehyde was excited with a UV laser to single rotational levels of the 4^3 and $2^4 4^1$ vibrational bands¹⁸ of S_1 in a pulsed supersonic free jet. Because nuclear spin is conserved during the dissociation,^{5,19} *para* and *ortho* H_2 (even and odd J) are produced by photolysis of *para* and *ortho* H_2CO (even and odd K_a). *Para* H_2CO was photolyzed on the $^7R_0(0)e$ line and *ortho* H_2CO was photolyzed on the $^6P_1(1)o$ line.²⁰ There was no evidence for saturation of the H_2CO transition, as the H_2CO fluorescence intensity was proportional to the photolysis laser power. The nascent H_2 (v, J) product was probed 50–100 ns after photolysis by vacuum-ultraviolet (VUV) laser-induced fluorescence (LIF) on the $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition. Figure 1 shows the three experimental geometries employed in this experiment. The jet axis, the laser propagation direction, and the fluorescence detection direction were mutually orthogonal. The polarizations of both the photolysis and probe lasers were linear with a degree of polarization greater than 94% as measured by a Glan-Thompson air spaced polarizer.

The correlations between the parent dipole moment μ , the H_2 rotational vector J , and the product velocity vector v

are extracted using Dixon's line shape analysis.^{14,21} If the fragments are assumed to have a delta function velocity distribution at v , then the LIF Doppler profile is given by¹⁴

$$g(\chi_D) = (2\Delta\nu_D)^{-1} [g_0 + g_2 P_2(\chi_D) + g_4 P_4(\chi_D) + g_6 P_6(\chi_D)], \quad (2)$$

where $\Delta\nu_D = \nu_0 v/c$ is the maximum Doppler shift (ν_0 is the line center and v is the average product velocity) and χ_D is the ratio of the Doppler shift to the maximum Doppler shift [$\chi_D = (v - \nu_0)/\Delta\nu_D$]. Additionally, $P_2(\chi_D)$, $P_4(\chi_D)$, and $P_6(\chi_D)$ are the second-, fourth-, and sixth-order Legendre polynomials.²² The g_i are functions of the renormalized bipolar moments $\beta_0^K(k_1 k_2)$ that describe the correlations between μ , v , and J .¹⁴

$$\begin{aligned} g_0 &= b_0 + b_1 \beta_0^2(02), \\ g_2 &= b_2 \beta_0^2(20) + b_3 \beta_0^0(22) + b_4 \beta_0^2(22) + b_5 \beta_0^2(24), \\ g_4 &= b_6 \beta_0^2(42) + b_7 \beta_0^0(44) + b_8 \beta_0^2(44), \\ g_6 &= b_9 \beta_0^2(64). \end{aligned} \quad (3)$$

Here, $b_0 \dots b_9$ are bipolar moment multipliers; they are calcu-

TABLE I. Bipolar moment multipliers $b_0 - b_9$ for the three geometries used in these experiments.^a

J	Geometry I		Geometry II		Geometry IV	
	R	P	R	P	R	P
1	1.1000	1.0000	1.1000	1.0000	0.8000	1.0000
	-0.2171	-1.6000	0.2629	0.8000	-0.0457	-1.6000
	-1.1000	-1.0000	-1.1000	-1.0000	-0.8000	-1.0000
	-0.1143	2.0000	-0.1143	2.0000	0.0571	2.0000
	-0.3755	-1.1429	0.3102	2.2857	-0.0327	-1.1429
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	-0.0441	-1.5429	0.1616	-0.5143	-0.0441	-1.5429
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	1.0667	1.0333	1.0667	1.0333	0.8667	0.9333
	-0.3602	-0.6395	0.3671	0.5034	-0.1524	-0.4354
	-1.0667	-1.0333	-1.0667	-1.0333	-0.8667	-0.9333
	-0.0173	0.3401	-0.0173	0.3401	0.1905	0.5442
	-0.5244	-0.7191	0.5145	0.9135	-0.1088	-0.3110
	0.0025	0.0133	0.0025	0.0133	0.0199	0.1066
	-0.1469	-0.4198	0.1647	0.0700	-0.1469	-0.4198
	-0.0087	-0.0466	-0.0087	-0.0466	-0.0262	-0.1399
	-0.0023	-0.0121	-0.0023	-0.0121	0.0136	0.0727
	0.0040	0.0212	0.0040	0.0212	0.0198	0.1060
8	1.0588	1.0412	1.0588	1.0412	0.8824	0.9176
	-0.4076	-0.5506	0.3949	0.4659	-0.1953	-0.3388
	-1.0588	-1.0412	-1.0588	-1.0412	-0.8824	-0.9176
	0.0318	0.2118	0.0318	0.2118	0.2441	0.4235
	-0.5641	-0.6655	0.5823	0.7866	-0.1395	-0.2420
	0.0033	0.0077	0.0033	0.0077	0.0263	0.0613
	-0.1883	-0.3267	0.1556	0.1089	-0.1883	-0.3267
	-0.0115	-0.0268	-0.0115	-0.0268	-0.0345	-0.0804
	-0.0030	-0.0070	-0.0030	-0.0070	0.0179	0.0418
	0.0052	0.0122	0.0052	0.0122	0.0261	0.0609

^a Appropriate for the R and P branches of a $\Sigma - \Sigma$ electronic transition. Collection of undispersed fluorescence is assumed and no nuclear spin effects are included.

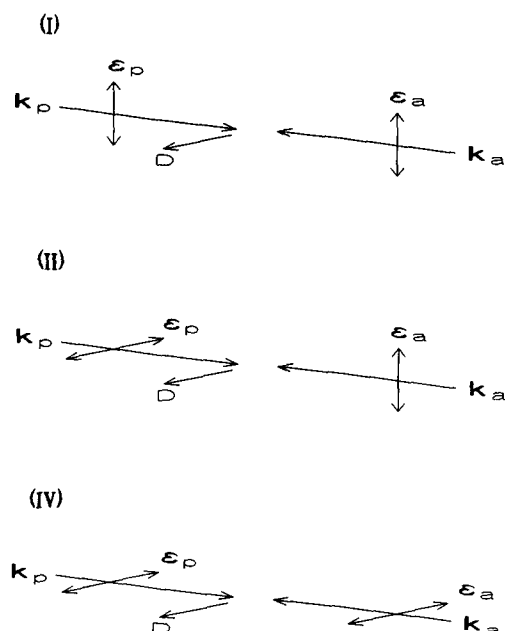


FIG. 1. The photolysis (k_p, ϵ_p) and probe (k_a, ϵ_a) laser beam geometries: k and ϵ are the laser propagation directions and polarizations; the detector D detects all polarizations. I is a mutually orthogonal geometry; II is the coaxially detected geometry with $\epsilon_a \perp \epsilon_p$; IV is the coaxially detected geometry with $\epsilon_a \parallel \epsilon_p$.

lated constants for a given fragment J , probed rotational transition, and experimental geometry. Table I lists the bipolar moment multipliers that are appropriate for the H_2 ($J = 1, 4, 8$) $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition for the three geometries used in this experiment. Hyperfine depolarization effects are not included. *Para* H_2 has no nuclear spin ($I = 0$) and hyperfine depolarization is negligible for *ortho* H_2 , which has $I = 1$.⁷

The line profiles have contributions from Legendre polynomials up to $P_6(\chi_D)$, but the $g_2P_2(\chi_D)$ is expected to dominate the structure of each line. This is because the bipolar moment multipliers for g_4 and g_6 are small compared to g_2 , and furthermore, the higher-order bipolar moments are expected to have a smaller magnitude than the lower-order moments.¹⁴ If the $g_4P_4(\chi_D)$ and $g_6P_6(\chi_D)$ terms are neglected, the line shape function is expressed as

$$g(\chi_D) = [I/(2\Delta\nu_D)] [1 + \beta_{\text{eff}} P_2(\cos \theta_a) P_2(\chi_D)]. \quad (4)$$

Here, I is the integrated peak intensity, β_{eff} is the effective line shape parameter, and θ_a is the angle between the photolysis polarization and the probe laser propagation axis. For the counterpropagating laser geometries used in these ex-

periments, θ_a is always 90° . The effective line shape parameter as expressed by Dixon is

$$\beta_{\text{eff}} = \left(\frac{b_2 \beta_0^2(20) + b_3 \beta_0^0(22) + b_4 \beta_0^2(22)}{[b_0 + b_1 \beta_0^0(02)] P_2(\cos \theta_a)} \right). \quad (5)$$

The alignment of the $\mathbf{J}$ vector in the lab frame is typically given by $A_0^{(2)}$ (Ref. 23) which equals $\frac{4}{3} \beta_0^2(02)$ in Dixon's analysis. The spatial anisotropy, often referred to as β , equals $2\beta_0^2(20)$. The other correlations in this analysis are the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation $\beta_0^0(22) = \langle P_2(\cos \omega'_{ir}) \rangle$, where ω'_{ir} is the angle between $\mathbf{v}$ and $\mathbf{J}$, and the $\langle \boldsymbol{\mu} \cdot \mathbf{v} \cdot \mathbf{J} \rangle$ correlation $\beta_0^2(22)$.

Both a P and an R branch for each H_2 (v, J) state were measured two to six times for three combinations of photolysis and probe laser polarizations. The line profiles were least-squares fit to the line shape function (which was convoluted to a Gaussian to account for initial parent velocities and the probe laser bandwidth⁷) to determine the intensity, maximum Doppler shift, and line shape parameter. Since our detection is unpolarized, each geometry is the average of two of Dixon's standard cases.¹⁴ The geometries shown in Fig. 1 correspond to his cases 1 and 2, 9 and 10, and 11 and 12.

TABLE II. The H_2 (v, J) vector correlations from photodissociation of $2^1 4^1 H_2CO$.^a

v	J	$A_0^{(2)b}$	β	$\beta_0^0(22)$	$\beta_0^2(22)$
<i>^rP₁(1) H₂CO</i>					
1	1	0.05 ± 0.06	0.04 ± 0.04 ^c	− 0.30 ± 0.02 ^c	0.00 ± 0.02 ^c
			− 0.01 ± 0.05	− 0.30 ± 0.02	− 0.01 ± 0.02
	3	0.17 ± 0.07	0.07 ± 0.04	− 0.21 ± 0.03	0.03 ± 0.03
			0.01 ± 0.04	− 0.21 ± 0.06	0.03 ± 0.03
3	1	0.04 ± 0.04	− 0.12 ± 0.07	− 0.28 ± 0.03	− 0.04 ± 0.03
	3	0.06 ± 0.04	− 0.08 ± 0.06	− 0.21 ± 0.08	− 0.07 ± 0.04
	5	0.05 ± 0.05			
	7	0.03 ± 0.11			
<i>^rR₀(0) H₂CO</i>					
1	0		0.52 ± 0.02 ^d		
			0.50 ± 0.02		
	2	− 0.15 ± 0.07	0.04 ± 0.03 ^c	− 0.20 ± 0.03	− 0.09 ± 0.02
			0.02 ± 0.03	− 0.18 ± 0.03	− 0.09 ± 0.02
	4	− 0.11 ± 0.07	− 0.16 ± 0.07	− 0.26 ± 0.09	− 0.10 ± 0.03
			− 0.15 ± 0.04	− 0.24 ± 0.07	− 0.10 ± 0.02
6		− 0.14 ± 0.11	0.02 ± 0.05	− 0.19 ± 0.10	− 0.02 ± 0.03
			− 0.01 ± 0.06	− 0.20 ± 0.11	− 0.02 ± 0.03
	8	− 0.16 ± 0.11	0.38 ± 0.12	− 0.12 ± 0.28	0.08 ± 0.07
3	0		0.85 ± 0.07 ^d		
	2	− 0.31 ± 0.06	0.41 ± 0.12 ^c	− 0.06 ± 0.12	− 0.04 ± 0.06
	4	− 0.20 ± 0.09	0.23 ± 0.14	− 0.08 ± 0.21	− 0.10 ± 0.08
	6	− 0.21 ± 0.13			

^aThe first entry for each rotational state corresponds to an analysis assuming a single recoil velocity; the second entry corresponds to the analysis assuming a Gaussian recoil velocity distribution with a fwhm equal to 14% of the average velocity.

^bFrom Ref. 7.

^cThe error bars in this column are twice the standard error from the least-squares fitting program.

^dThe error bars are ± 2 standard deviations of the mean.

TABLE III. The H_2 (v, J) vector correlations from photodissociation of $4^3 H_2CO$.

v	J	$A_0^{(2)a}$	β	$\beta_0^0(22)$	$\beta_0^2(22)$
$^nP_1(1) H_2CO$					
1	1	0.00 ± 0.07	-0.10 ± 0.05^b	-0.16 ± 0.02^b	0.01 ± 0.02^b
	3	0.05 ± 0.07	-0.09 ± 0.04	-0.23 ± 0.04	0.02 ± 0.02
	5	0.10 ± 0.16	-0.05 ± 0.06	-0.23 ± 0.16	0.00 ± 0.04
	7	0.08 ± 0.16			
$^nR_0(0) H_2CO$					
1	0		-0.35 ± 0.03^c		
	2	-0.05 ± 0.06	-0.41 ± 0.04^b	-0.28 ± 0.03	-0.22 ± 0.02
	4	-0.11 ± 0.08	-0.34 ± 0.05	-0.30 ± 0.07	-0.29 ± 0.03
	6	-0.24 ± 0.11	-0.23 ± 0.07	-0.25 ± 0.13	-0.31 ± 0.04
3	0		-0.36 ± 0.10^c		

^a From Ref. 7.^b The error bars in this column are twice the standard error from the least-squares fitting program.^c The error bars are ± 2 standard deviations of the mean.

The alignment $[\beta_0^2(02) = \frac{5}{4} A_0^{(2)}]$ was determined from integrated line intensities⁷ and was used as an input into Eq. (5). The set of six Doppler line shapes for each H_2 (v, J) yield six separate values of β_{eff} that are converted into three bipolar moments via a least-squares fit to the solution of a set of over-determined simultaneous solutions. Tables II and III list all of the product H_2 spatial anisotropies, $\langle \mathbf{v} \cdot \mathbf{J} \rangle$, and $\langle \mu \cdot \mathbf{v} \cdot \mathbf{J} \rangle$ correlations measured in these experiments: H_2 ($v = 1$) from 4^3 and $2^1 4^1 S_1$ H_2CO photolysis, and H_2 ($v = 3$) from $2^1 4^1 S_1$ H_2CO .

It has been assumed that the fragment velocity distribution is well approximated as a single velocity. The H_2 ($v = 1$) data for the $2^1 4^1$ photolysis are reanalyzed using the broadest possible fragment velocity distribution to determine the effect of neglecting the velocity distribution. The broadest H_2 velocity distribution would result from an uncorrelated H_2/CO product quantum state distribution. The H_2 ($v = 1, J$) velocity distributions are constructed by assuming that the H_2 ($v = 1, J$) state is correlated with a Gaussian distribution of CO J states with a peak at $J_{\text{CO}} = 42$, a full width half-maximum (fwhm) of 20, and a $CO(v = 1)/CO(v = 0)$ population ratio of 0.10. This $CO(v, J)$ distribution closely matches the measured distribution from Ref. 3. The resulting H_2 ($v = 1, J$) velocity distributions are approximately Gaussian with a fwhm equal to 0.14 of the peak velocity. The H_2 ($v = 1, J$) Doppler line shapes are reanalyzed with the inclusion of this Gaussian fragment velocity distribution. These vector correlation results are compared to the single fragment velocity results in Table II. Table II clearly shows that the single fragment velocity approximation is quite good in this experiment.

III. DISCUSSION

A. Bipolar moment interpretation

Three methods have recently been developed to describe how the shape of a fragment LIF Doppler profile depends on the correlations between the parent absorption dipole moment μ , the fragment rotational vector J , and the fragment velocity vector v .^{14,16,17} One approach, developed by Hall *et al.*,¹⁷ uses classical mechanics to calculate Doppler profiles for any spatial anisotropy and limiting values of the other vector correlations (e.g., $v \perp J$ and $v \parallel \mu$). This approach is only valid in the limit of high fragment J (J greater than 10, perhaps) and is not expected to be suitable for analyzing low- J H_2 peak shapes from the photodissociation of H_2CO . The second approach, also developed by Hall *et al.*, uses the quantum mechanical density matrix method,^{16,17} which is good for all values of J , but is computationally time consuming at high J .

Dixon has developed a third approach that is based on the semiclassical expansion of the correlated angular momentum and velocity distribution in terms of the expectation values of bipolar harmonics.^{14,21} The methods of Hall *et al.* are ideal for calculating line shapes for a given (known) set of vector correlations, but Dixon's method allows one (in principle) to invert measured Doppler profiles to obtain the bipolar moments which describe the vector correlations. However, it is not entirely clear whether Dixon's analysis is valid for fragments with low J .

Therefore, before discussing the physical significance of the measured bipolar moments, it is prudent to discuss the validity of Dixon's analysis at low J . This is done by compar-

ing line shapes calculated with Dixon's analysis for an assumed spatial anisotropy and $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation to line shapes calculated using the density matrix quantum method described by Hall *et al.*^{16,17} The calculation is for a prompt dissociation (no parent rotations prior to dissociation) and a single fragment recoil velocity is assumed. In order to simplify the density matrix quantum calculation, the calculations are performed for the case of $\mathbf{J}$ being azimuthally symmetric about $\mathbf{v}$. This is equivalent to having a diagonal density matrix when $\mathbf{v}$ is the axis of quantization.

The expectation values for the bipolar moments in the limit of high fragment J and prompt dissociation are¹⁴

$$\begin{aligned}\beta &= 2\beta_0^2(20) = 2\langle P_2(\cos \theta'_i) \rangle, \quad -1 \leq \beta \leq 2; \\ \beta_0^0(22) &= \langle P_2(\cos \omega'_{ir}) \rangle, \quad -\frac{1}{2} \leq \beta_0^0(22) \leq 1; \\ \beta_0^2(22) &= \langle -P_2(\cos \theta'_i) P_2(\cos \theta'_r) \\ &\quad - \frac{3}{8} \sin 2\theta'_i \sin 2\theta'_r \cos(\phi'_i - \phi'_r) \\ &\quad + (\frac{3}{4}) \sin^2 \theta'_i \sin^2 \theta'_r \cos[2(\phi'_i - \phi'_r)] \rangle, \\ &\quad -\frac{1}{2} \leq \beta_0^2(22) \leq 1.\end{aligned}\quad (6)$$

The vectors $\mathbf{v}$, $\mathbf{J}$, and $\boldsymbol{\mu}$ are defined in the body-fixed coordinate system, where z is along $\boldsymbol{\mu}$ (the parent transition dipole). The polar angle between $\mathbf{v}$ and $\boldsymbol{\mu}$ is θ'_i , the polar angle between $\mathbf{J}$ and $\boldsymbol{\mu}$ is θ'_r , and the angle between $\mathbf{v}$ and $\mathbf{J}$ is ω'_{ir} . The angles ϕ'_i and ϕ'_r are the azimuthal angles for $\mathbf{v}$ and $\mathbf{J}$. The spatial anisotropy of the fragments β indicates the tendency of $\mathbf{v}$ to be along $\boldsymbol{\mu}$ (positive value) or perpendicular to $\boldsymbol{\mu}$ (negative value). The bipolar moment $\beta_0^2(22)$ describes the triple vector correlation $\langle \boldsymbol{\mu} \cdot \mathbf{v} \cdot \mathbf{J} \rangle$. Both β and $\beta_0^2(22)$ involve $\boldsymbol{\mu}$ and their values will be decreased by parent rotation.

Here, $\beta_0^0(22)$ is the second Legendre moment of the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation. It is independent of the laboratory frame because both $\mathbf{v}$ and $\mathbf{J}$ are defined relative to the molecule fixed axis system by the fragmentation dynamics. It reflects the tendency of $\mathbf{J}$ to be parallel or antiparallel to $\mathbf{v}$ (positive value), or perpendicular to $\mathbf{v}$ (negative value).

The bipolar moments need to be determined for low J in order to compare Dixon's analysis with the density matrix approach. The strategy that is used here is to use the vectorial model of angular momentum; i.e., treat the angular momentum as a vector $\mathbf{J}$ with magnitude $[J(J+1)]^{1/2}$ that precesses around $\mathbf{v}$ at an angle of ω'_{ir} , where

$$\cos \omega'_{ir} = M_v / [J(J+1)]^{1/2}. \quad (7)$$

Here, M_v is the projection of $\mathbf{J}$ onto $\mathbf{v}$. The angle between $\boldsymbol{\mu}$ and $\mathbf{J}$ is defined in the same manner. The expectation values of the bipolar moments are obtained by substituting the expressions for $\cos \omega'_{ir}$ and $\cos \theta'_r$ into the semiclassical arguments and summing over the appropriately weighted M distribution. For example, the expectation value for $\beta_0^0(22)$ is

$$\langle P_2(\cos \omega'_{ir}) \rangle = \sum_{M_v} \left(\frac{3M_v^2}{2J(J+1)} - \frac{1}{2} \right) P(M_v), \quad (8)$$

where $P(M_v)$ is the population of the M_v level and $\sum P(M_v) = 1$. Equation (8) is exact, but the analogous expressions for the higher-order Legendre polynomials are only valid in the limit of high J .²⁴ The M_z distribution, where

TABLE IV. Expectation values of the bipolar moments for some limiting values of the spatial anisotropy β and $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation for fragments with $J = 1$.^a

	$\beta = 2$		$\beta = 0$		$\beta = -1$	
	$\mathbf{v} \parallel \mathbf{J}^b$	$\mathbf{v} \perp \mathbf{J}^c$	$\mathbf{v} \parallel \mathbf{J}$	$\mathbf{v} \perp \mathbf{J}$	$\mathbf{v} \parallel \mathbf{J}^d$	$\mathbf{v} \perp \mathbf{J}^e$
$\beta_0^2(02)$	$\frac{1}{4}$ (1)	$-\frac{1}{2}$ ($-\frac{1}{2}$)	0 (0)	0 (0)	$-\frac{1}{8}$ ($-\frac{1}{2}$)	$\frac{1}{4}$ ($\frac{1}{4}$)
$\beta_0^2(20)$	1 (1)	1 (1)	0 (0)	0 (0)	$-\frac{1}{2}$ ($-\frac{1}{2}$)	$-\frac{1}{2}$ ($-\frac{1}{2}$)
$\beta_0^0(22)$	$\frac{1}{4}$ (1)	$-\frac{1}{2}$ ($-\frac{1}{2}$)	$\frac{1}{4}$ (1)	$-\frac{1}{2}$ ($-\frac{1}{2}$)	$\frac{1}{4}$ (1)	$-\frac{1}{2}$ ($-\frac{1}{2}$)
$\beta_0^2(22)$	$-\frac{1}{4}$ (-1)	$\frac{1}{2}$ ($\frac{1}{2}$)	0 (0)	0 (0)	$\frac{1}{8}$ ($\frac{1}{2}$)	$-\frac{1}{4}$ ($-\frac{1}{4}$)
$\beta_0^2(24)$	... (1)	... ($\frac{3}{8}$)	... (0)	... (0)	... ($-\frac{1}{2}$)	... ($\frac{1}{16}$)
$\beta_0^2(42)$	$\frac{1}{4}$ (1)	$-\frac{1}{2}$ ($-\frac{1}{2}$)	0 (0)	0 (0)	$-\frac{1}{8}$ ($-\frac{1}{2}$)	$\frac{1}{4}$ ($\frac{1}{4}$)
$\beta_0^0(44)$	... (1)	... ($\frac{3}{8}$)	... (1)	... ($\frac{3}{8}$)	... (1)	... ($\frac{3}{8}$)

^a Axial symmetry of $\mathbf{J}$ around $\mathbf{v}$ is assumed. The values in parenthesis are the bipolar moment values in the high J limit; they are listed in Fig. 3 of Ref. 14.

^b Corresponds to case (a) of Fig. 3 in Ref. 14.

^c Corresponds to case (b) of Fig. 3 in Ref. 14.

^d Corresponds to case (d) of Fig. 3 in Ref. 14.

^e Corresponds to the average of cases (c) and (e) of Fig. 3 in Ref. 14.

M_z is the projection of $\mathbf{J}$ onto the body-fixed z axis (defined to be along $\boldsymbol{\mu}$), is related to $P(M_v)$ by (Ref. 25, p. 91)

$$P(M_z) = \sum_{M_v} [d_{M_z M_v}^J(\theta'_i)]^2 P(M_v),$$

where $d_{M_z M_v}^J(\theta'_i)$ is a Wigner rotation matrix element.^{25,26}

Table IV lists the calculated bipolar moment expectation values for several limiting correlations of $\boldsymbol{\mu}$, $\mathbf{v}$, and $\mathbf{J}$ for a fragment with $J = 1$ and for a fragment in the high J limit. The corresponding $P(1)$ and $R(1)$ LIF Doppler line shapes appropriate for a Σ - Σ electronic transition and geometry I (see Fig. 1) are shown as lines in Fig. 2. The symbols in Fig. 2 are the equivalent calculation using the density matrix quantum approach. The line shapes calculated using Dixon's analysis agree exactly with the line shapes from the density matrix approach for every case in Fig. 2. Dixon's analysis is expected to be equally valid in the case of a general photofragmentation (such as H_2CO), where the fragment $\mathbf{J}$ is not expected to be azimuthally symmetric about $\mathbf{v}$.

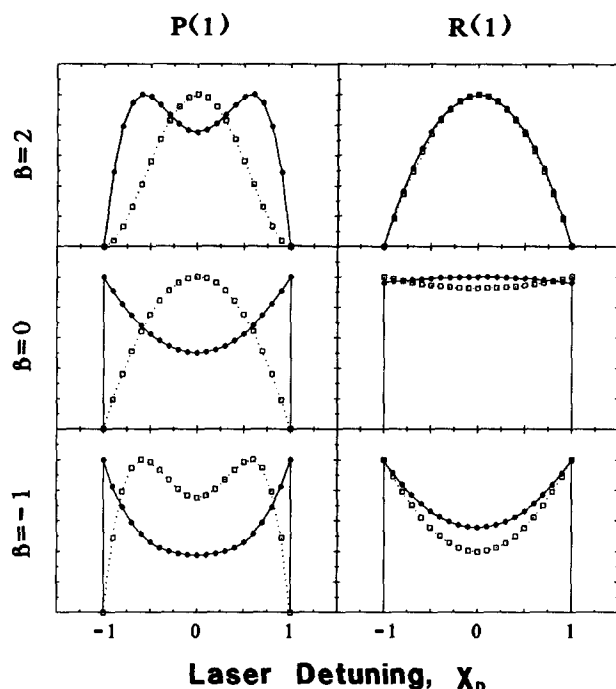


FIG. 2. The $P(1)$ and $R(1)$ Doppler profiles appropriate for a parallel electronic transition using geometry I. The parameter β describes the fragment recoil spatial anisotropy. The lines are the prediction of Dixon's analysis while symbols are the prediction of the density matrix approach. Solid lines and circles are for the limiting case of $\mathbf{v} \parallel \mathbf{J}$ and the dotted lines and open squares are for the limiting case of $\mathbf{v} \perp \mathbf{J}$. All amplitudes have been normalized to equal heights.

B. $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation

Some discussion is needed on our ability to measure the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation using the H_2 $B-X$ transition, which only has P and R branches. At high J (say greater than $J = 6$), the P and R branch of a given J have virtually the same line shape. It becomes very difficult to distinguish effects due to the spatial anisotropy from the effects due to the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation. Measuring a Q -branch line greatly helps because the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation changes the line profiles in the opposite sense from P and R branches. Similarly, one could measure the profiles with the probe propagation direction along the photolysis electric vector; this would aid in separating the effects of β from the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation. However, as Fig. 2 shows, P - and R -branch line profiles are very different for a given $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation at low J . The inability to discriminate the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation from the spatial anisotropy in this experiment at higher fragment J is seen in the larger error bars for H_2 ($v = 1, J = 8$) in Table II.

Figure 3 shows the $P(1)$ and $R(1)$ H_2 ($v = 1$) line profiles measured using geometry I. The simulated line profiles have a β_{eff} calculated with Eq. (5) using the measured values of the bipolar moments. The calculated β_{eff} agree well with the β_{eff} obtained by finding the best fit parameters for each individual line. The difference in the measured $P(1)$ and $R(1)$ H_2 line shapes clearly shows that the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation, $\beta_0^0(22)$, is negative. The values of $\beta_0^0(22)$ are, within the error bars, constant as a function of H_2 (v, J) and

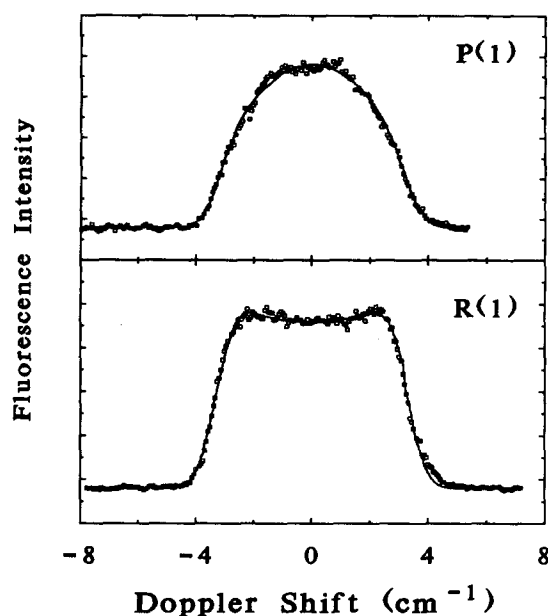


FIG. 3. The H_2 ($v = 3, J = 1$) Doppler profiles from photolysis on the $^oP_1(1) \leftarrow 2^14^1 S_1$ H_2CO line. Both lines are measured on the $B-X$ ($0,3$) line using geometry I. The simulated line shapes correspond to the bipolar moments listed in Table II and $v = 1.28 \times 10^6$ cm/s. The lines are normalized to unit height.

photolysis transition. The weighted average for all of the H_2 (v, J) fragments measured is $\beta_0^0(22) = -0.23 \pm 0.02$ which is closer to the limit of $\mathbf{v} \perp \mathbf{J}$ [$\beta_0^0(22) = -0.5$] than to $\mathbf{v} \parallel \mathbf{J}$ [$\beta_0^0(22) = 0.25$ for $J = 1$ and $\beta_0^0(22) = 1.0$ for high J].

C. Spatial anisotropy

Formaldehyde predissociates and the lifetime of the excited state is long ($2^14^1 S_1$, $\tau \approx 50$ ns) compared to the parent rotational period. The many parent rotations prior to dissociation are expected to reduce the laboratory frame correlations that are the rotational alignment $A_0^{(2)}$, the spatial anisotropy β , and the $\langle \mu \cdot \mathbf{v} \cdot \mathbf{J} \rangle$ correlation $\beta_0^2(22)$.

In particular, the laboratory frame correlations from photolysis on the $^oP_1(1) \leftarrow o$ line should be zero because the excited state parent molecule has $J = 0$, and therefore, its rotational wave function is isotropic. Tables II and III show that the $A_0^{(2)}$, β , and $\beta_0^2(22)$ values measured for this photolysis are near zero, which is a good indication that there are no gross systematic errors in this experiment. One potential systematic error is that the $^oP_1(1) \leftarrow o$ H_2CO line is not resolved from the $^oQ_1(3) \leftarrow e$ line. At the measured H_2CO rotational temperature of 5 K, photolysis of the $^oQ_1(3) \leftarrow e$ line accounts for 10% of the products.

Figure 4 shows the H_2 ($v, J = 0$) line shapes for photolysis on the $R_0(0) \leftarrow e$ line of 2^14^1 and 4^3 H_2CO . The H_2 ($J = 0$) has no $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation and the line shapes directly reflect the spatial anisotropy β . For the experimental geometries employed here, round lines correspond to a positive anisotropy and dipped lines to a negative anisotropy. Figure 4 clearly shows that the anisotropy is sensitive to the S_1 H_2CO vibrational state.

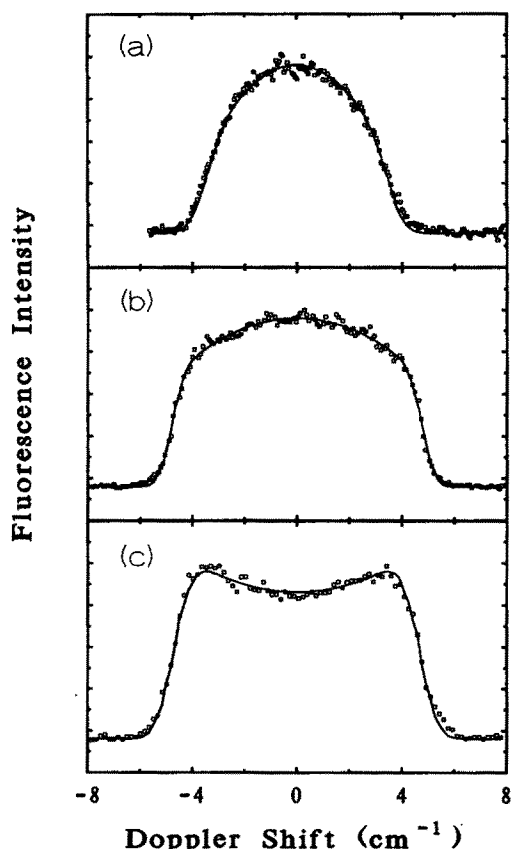


FIG. 4. The H_2 $R(0)$ Doppler line shapes for photolysis on the $\text{R}_0(0)e$ line. (a) H_2 ($v=3$) from $2^1 4^1 S_1$ H_2CO photolysis measured on the $B-X$ (0,3) band. The simulated line shape has $\beta = 0.85$. (b) H_2 ($v=1$) from $2^1 4^1 S_1$ photolysis measured on the $B-X$ (3,1) band. The simulated line shape has $\beta = 0.52$. (c) H_2 ($v=1$) from $4^3 S_1$ H_2CO photolysis measured on the $B-X$ (3,1) band. The simulated line shape has $\beta = -0.35$. The peaks are normalized to unit height.

Figure 5 shows the spatial anisotropy as a function of the H_2 (v, J) state for photolysis on the $\text{R}_0(0)$ line of $2^1 4^1$ and $4^3 S_1$ H_2CO . In the $2^1 4^1$ photolysis, the anisotropy parameter has a large J dependence, and β for H_2 ($v=3$) is

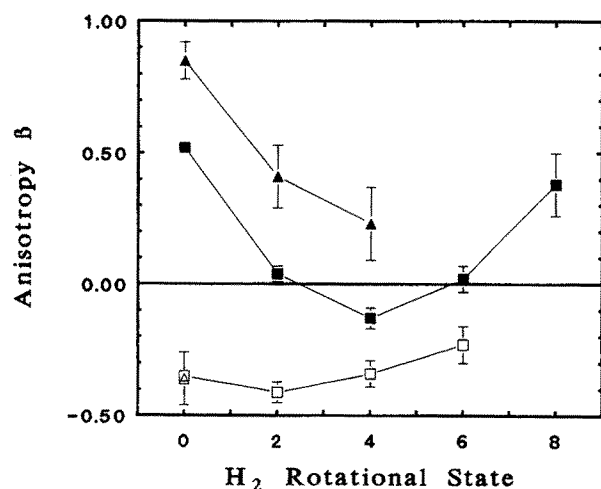


FIG. 5. The H_2 spatial anisotropies for $\text{R}_0(0)e$ ($1_{11}, -0_{00}$) excitation to different vibrational states of S_1 H_2CO . Solid symbols are for $2^1 4^1$ photolysis and hollow symbols are for 4^3 photolysis; squares and triangles are for H_2 ($v=1$) and H_2 ($v=3$), respectively.

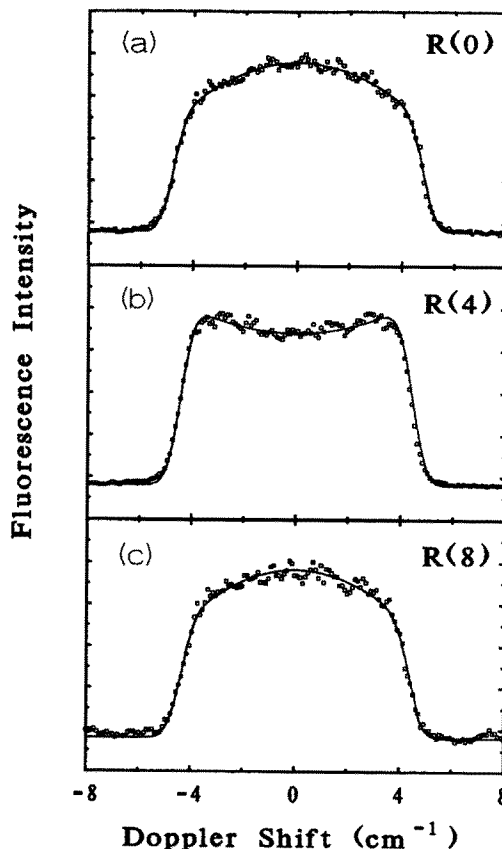


FIG. 6. The H_2 ($v=1$) $R(0)$, $R(4)$, and $R(8)$ line profiles for photolysis on the $2^1 4^1 \text{R}_0(0)e$ line using geometry I. (a) $R(0)$ measured on the $B-X$ (3,1) band; the simulated line shape has $\beta_{\text{eff}} = 0.52$. (b) $R(4)$ measured on the $B-X$ (2,1) band; the simulated line shape has $\beta_{\text{eff}} = -0.25$. (c) $R(8)$ measured on the $B-X$ (4,1) band; the simulated line shape has $\beta_{\text{eff}} = 0.48$. The simulations assume a single recoil velocity and the peaks are normalized to unit height.

greater than for H_2 ($v=1$) by about 0.3 for all of the J measured. Figure 6 shows the $R(0)$, $R(4)$, and $R(8)$ H_2 ($v=1$) line profiles for the $2^1 4^1 \text{R}_0(0)$ photolysis. The R -branch line shapes are most sensitive to the spatial anisotropy (see for example Fig. 2) and Fig. 6 clearly shows that β is relatively large and positive for H_2 ($v=1, J=0$) and H_2 ($v=1, J=8$) while it is small (and slightly negative) for H_2 ($v=1, J=4$). As a further check of the anisotropy trend with H_2 J -state, the H_2 ($v=1$) data were reanalyzed with a fixed anisotropy equal to the value measured for H_2 ($v=1, J=0$) ($\beta = 0.52$). The least-squares fit has large positive $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlations [$\beta_0^0(22) \approx 0.6$] and the fits to the line shapes are extremely poor. The spatial anisotropy J dependence from photolysis to $4^3 S_1$ H_2CO is different from the $2^1 4^1$ photolysis. The anisotropy has a much smaller H_2 J dependence and β is the same for H_2 ($v=1, J=0$) and H_2 ($v=3, J=0$) (which was the only H_2 ($v=3$) J state measured for the 4^3 photolysis).

One can only speculate on the observed trend of β with fragment J for the $2^1 4^1 \text{R}_0(0)$ photolysis.⁶ In the framework of an impulsive model, the peak of the H_2 product state distributions is determined by the transition-state geometry and the width arises from motions in the transition-state nor-

mal modes. The $J = 0$ and $J = 8$ populations are small since there are only a few special transition-state geometries and momenta which produce H_2 in low or high rotational states.⁶ The H_2 products from these special geometries must have a large and positive anisotropy. However, the populations in $J_{H_2} = 2-6$ are considerably larger. There are many transition-state motions that lead to intermediate rotational states with a corresponding distribution of recoil velocity directions. This causes a reduction of the observed anisotropy. As a result, the anisotropy is larger for the extremes of the distribution and reduced for the majority of the rotational product states. However, this idea is not substantiated by the simplest execution of this model (see Sec. III D.).

Furthermore, the strong dependence of the anisotropy parameter on J_{H_2} for photolysis on the $2^1A' R_0(0)$ line may be anomalous. The $R(0)$ and $P(4)$ H_2 ($v = 1$) Doppler profiles were measured for photolysis to several different $2^1A'$ rotational levels.²⁷ The only photolysis line that produced a tremendous difference in the $R(0)$ and $P(4)$ line shapes was the $^1R_0(0)$ line, which is a strong indication that the anisotropy difference between fragments with $J = 0$ and $J = 4$ is not so great for photolysis on the other lines. Profiles for different geometries were not obtained, so a complete quantitative analysis of the vector correlations is not available.

The spatial anisotropies reported here are measured in the laboratory frame. Ideally, we want to learn about the dynamics in the molecule-fixed frame which can be accomplished by deconvoluting the effects of parent rotation on the measured anisotropy parameter. The effects of parent rotation of fragment anisotropy have been treated using classical mechanics by Jonah²⁸ for linear molecules, and by Yang and Bersohn²⁹ for symmetric tops. Both of these treatments average over a Boltzmann distribution of parent rotational states. For linear molecules with lifetimes τ long compared to the parent rotational period, the fragment anisotropy is reduced by a factor of 4.^{28,29} The analysis for a symmetric top is much more complicated. If the transition dipole is along the top axis, the anisotropy as $\tau \rightarrow \infty$ is reduced by a factor of 4 to 6.²⁹ For excitation on a b -type transition of formaldehyde, Yang and Bersohn's theory predicts that the fragment anisotropy limits are $-0.18 < \beta < 0.09$.

In this work, H_2 anisotropies as high as $\beta = 0.8$ and as low as -0.35 have been measured, which is outside the range of the classical models ($-0.18 < \beta < 0.09$). Clearly, the classical approximations, which are applicable for parent molecules excited to high rotational states, and averaging over the parent rotational Boltzmann distribution, is not suitable for the well-defined and very low formaldehyde rotational states ($J = 1$) accessed in these experiments. Here, a model is presented where a parent molecule is excited to a well-defined rovibrational state in S_1 . This state internally converts to a highly excited vibrational state of S_0 that dissociates over a steep repulsive barrier. The dissociation is considered to be impulsive such that the fragment kinetic energy is much larger than the rotational kinetic energy of the parent. The fragment recoil anisotropy measured in the lab frame is then a convolution of the distribution of the parent molecule-fixed axis frame in space at the instant of the dissociation and the recoil distribution of the fragments in the

molecular frame. The fragment recoil distribution in the molecular frame is governed by the dynamics of the photodissociation.

Formaldehyde is a near-prolate, slightly asymmetric top. Symmetric top rigid rotor wave functions $\psi_{J,K_a,K_c,M}$ are used to describe the rotational states. Here, K_a and K_c are labels that represent the projection of J on the molecular symmetry axis in the prolate and oblate symmetric top limits; M is the projection of J on the space-fixed axis of quantization, which is defined to be along the electric vector of the linearly polarized dissociation light. Excitation of the $2^1A'$ and 4^3 bands of S_1 are b -type transitions; i.e., the transition dipole μ is in the plane of the molecule and perpendicular to the CO axis. The excitation light aligns μ , not the symmetry axis, so the wave function will be expressed in a type II' representation ($x \leftrightarrow c, y \leftrightarrow a, z \leftrightarrow b$) (Ref. 25, p. 268) so that the molecule-fixed z axis is along the transition dipole. Excitation of the $^1R_0(0)e$ line ($1_{11} \leftarrow 0_{00}$) produces only the $M = 0$ level in S_1 due to the $\Delta M = 0$ dipole selection rule. The rigid rotor wave function for the 1_{11} ($M = 0$) level in the II' representation is

$$\psi_{1,1,1,0} = |100\rangle,$$

where $|JKM\rangle$ represents the normal symmetric top wave function²⁵

$$|JKM\rangle = [(2J+1)/8\pi^2]^{1/2} D_{MK}^{J*}(\phi, \theta, \chi), \quad (9)$$

where $D_{MK}^J(\phi, \theta, \chi)$ is a Wigner rotation matrix element and ϕ , θ , and χ are the three Euler angles relating the body-fixed and space-fixed axis frames.³⁰

RRKM calculations that include tunneling corrections show that the rate of dissociation of S_0 H_2CO excited to the energies of this experiment ($\approx 1700 \text{ cm}^{-1}$ above the barrier) is slow ($\approx 600 \text{ ps}$)^{31,32} with respect to the H_2CO classical rotational period. This implies that the appropriate rotational levels and wave functions to be used in the model will correspond to H_2CO on the S_0 surface near the transition state. Polik *et al.*^{32,33} have shown that K_a is an "almost good" quantum number in S_0 D_2CO at energies near the barrier to dissociation. If K_a is considered a good quantum number, then the selection rules for internal conversion are $\Delta J = 0$, $\Delta K = 0$, and $\Delta M = 0$.^{34,35} That is, the symmetric top wave function $|100\rangle$ also describes the rigid rotor wave function in S_0 .

The probability $P_{J,K_a,K_c,M}(\phi, \theta, \chi)$ of finding the asymmetric top z axis pointing into the solid angle element $d\Omega = d\phi \sin \theta d\theta d\chi$ is

$$P_{J,K_a,K_c,M}(\phi, \theta, \chi) d\Omega = |\psi_{J,K_a,K_c,M}|^2 d\Omega. \quad (10)$$

The explicit form of $P_{J,K_a,K_c,M}$ for the 1_{11} ($M = 0$) rotational level is

$$\begin{aligned} P_{1,1,1,0}(\phi, \theta, \chi) &= [3/(8\pi^2)] |D_{00}^{1*}(\phi, \theta, \chi)|^2 \\ &= [3/(8\pi^2)] \cos^2 \theta. \end{aligned} \quad (11)$$

This $\cos^2 \theta$ distribution is the same as the distribution parent axes have in a prompt dissociation. This simple model predicts that the limits on the anisotropy, as well as the other laboratory frame correlations, for photolysis on the $^1R_0(0)e$ line are equal to the limits for a prompt dissociation, which

are given in Eq. (6). A generalized version of this model that is appropriate for parent excitation on an arbitrary rotational transition has been formulated and is presented elsewhere.^{36,37}

The anisotropy measured for the H_2 ($v = 1, J = 0$) fragment for $2^1 4^1 S_1$ $\text{H}_2\text{CO} \rightarrow R_0(0)$ photolysis is $\beta = 0.52$. According to the model, $\beta = 2 \langle P_2(\cos \theta'_i) \rangle$, which implies that $\langle P_2(\cos \theta'_i) \rangle = 0.26$, $\langle \cos^2 \theta'_i \rangle = 0.51$ and the distribution of θ'_i is centered about 45° . For H_2 ($v = 3, J = 0$), $\beta = 0.85$, $\langle \cos^2 \theta'_i \rangle = 0.62$ and $\theta'_i \approx 38^\circ$. The same parameters for H_2 ($v = 1$ and $3; J = 0$) from photolysis on the $4^3 \rightarrow R_0(0)e$ line are $\beta = -0.35$, $\langle \cos^2 \theta'_i \rangle = 0.22$ and 62° .

It is surprising that the fragment spatial anisotropies for photolysis on the $\rightarrow R_0(0)e$ line of the 4^3 and $2^1 4^1$ bands are so different. One possible cause is Coriolis coupling in S_1 . The K structure of the 4^3 band is perturbed at higher K values by an a -type Coriolis interaction between the 4^3 and 6^1 levels.³⁸ This would cause the transition dipole to have a component along the c axis as well as the b axis. This would increase the value of θ'_i and reduce the measured anisotropy. However, a calculation using the known selection rules and a typical coupling constant ($\zeta^a = 10 \text{ cm}^{-1}$)³⁹ shows that the 6^1 vibrational level contributes less than 5% to the $4^3 1_{11}$ level wave function. The $2^1 4^1$ band has a perturbation due to a b -type Coriolis interaction with the 3^1 level.^{40,41} Once again, a simple calculation using the known selection rules and matrix coupling elements⁴⁰ shows that the 3^1 vibrational level contribution to the $2^1 4^1 1_{11}$ level wave function is less than 1%.

The 4^3 and $2^1 4^1$ bands are also perturbed by singlet-triplet interactions.^{38,41} The coupling matrix elements are small ($0.01\text{--}0.10 \text{ cm}^{-1}$)³⁸ and in general, only a few rotational levels of a given S_1 vibrational level are coupled to adjacent triplet rovibronic levels. None of the rotational levels that show magnetic activity due to singlet-triplet mixing can be assigned to the $4^3 1_{11}$ level³⁸ and the $2^1 4^1 1_{11}$ level is not known to show magnetic activity.⁴¹

Another possibility is that the dissociation dynamics for the different vibrational levels in S_0 are different. The various S_1 rotational levels are at different energies and almost surely couple to different vibrational levels of S_0 . Polik *et al.*^{32,33} have shown that the highly excited vibrational states of S_0 D_2CO are strongly mixed at energies near the dissociation threshold; i.e., the basis function coefficients of the S_0 eigenstates are Gaussian random when the eigenstates are projected onto harmonic oscillator basis functions. However, quantum statistical fluctuations result in a large S_0 level-to-level variation of properties (e.g., lifetimes).^{32,33} This could result in different product state distributions and vector correlations for different photolyses. A more direct method to observe state-specific effects in the "lumpy continuum" of S_0 is to measure CO rotational distributions or H_2 vibrational distributions for photolysis to different S_1 rotational levels of a given vibrational band. Such experiments are now under way and preliminary results show that the peak of the J_{CO} distribution shifts for photolysis to different $2^1 4^1 S_1$ rotational states.⁴² A change in the H_2 ($v = 1$)/ H_2 ($v = 3$) ratio for different photolyses in the $2^1 4^1$ band has also been observed.³⁶

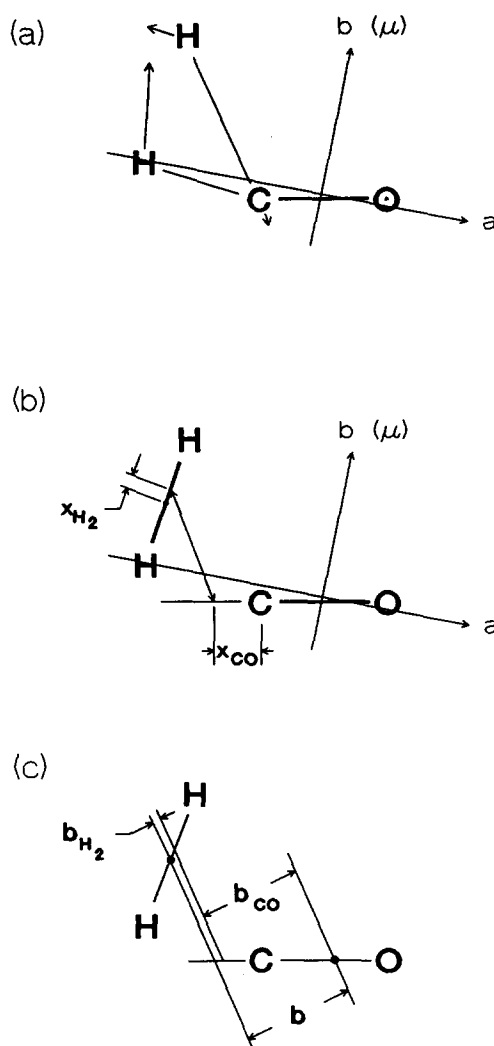


FIG. 7. (a) The *ab initio* transition-state geometry and reaction coordinate.^{8,9} The inertial a and b axes are also shown. (b) The parameters used in the semiclassical impulsive model calculation. (c) The "effective impact parameters" b_{H} and b_{CO} ; b is the impact parameter for the reaction. The points represent the H-H and CO centers of mass.

D. Impulsive model

The same impulsive model that successfully describes the H_2 and CO rotational distributions and the H_2/CO product quantum state correlations⁷ is used to calculate the vector correlations. The model is similar to Levene and Valentini's model⁴³ and has previously been described in detail.⁷ The model combines the vibrational motions of the parent molecule with the modified impulsive model⁴⁴ as applied to a planar tetra-atomic. Because H_2CO predissociates, a geometry between the transition state and products is used instead of the traditional ground state geometry. Figure 7(a) shows Goddard and Schaefer's *ab initio* transition-state geometry and reaction coordinate for the molecular dissociation of H_2CO .⁸⁻¹⁰ The transition-state geometry is planar and bent and the reaction coordinate suggests a large impact parameter as has been experimentally observed.^{5,7} In the model, the impulse is applied between a point along the H-H line and a point along the CO line outside of the C nucleus. Fig-

ure 7 shows the relevant parameters.

The energy available to be partitioned between product rotation and product translation is E'_{avl} and is equal to the

$$E_{CO}^{rot} = \frac{E'_{avl}}{1 + [\mu_{CO}\tilde{r}_{CO}^2/\mu_{H_2-CO}b_{CO}^2] + [\mu_{CO}\tilde{r}_{CO}^2b_{H_2}^2/\mu_{H_2}\tilde{r}_{H_2}^2b_{CO}^2]}, \quad (12)$$

where μ_{CO} and μ_{H_2} are the reduced masses of CO and H_2 and μ_{H_2-CO} is the reduced mass of H_2-CO [$=m_{H_2}m_{CO}/(m_{H_2}+m_{CO})$]. The "effective AB impact parameter" b_{AB} is the shortest distance from the AB center of mass to the line along the impulsive force [see Fig. 7(c)]. The H_2 rotational energy is calculated from

$$\frac{E_{H_2}^{rot}}{E_{CO}^{rot}} = \frac{\mu_{CO}\tilde{r}_{CO}^2b_{H_2}^2}{\mu_{H_2}\tilde{r}_{H_2}^2b_{CO}^2} = \frac{B_{H_2}b_{H_2}^2}{B_{CO}b_{CO}^2}, \quad (13)$$

where B_{H_2} and B_{CO} are the rotational constants for the ap-

propriate vibrational states of the product H_2 and CO. The magnitude of the H_2 angular momentum j_{H_2} is given by

$$j_{H_2}/\hbar = (E_{H_2}^{rot}/B_{H_2})^{1/2}. \quad (14)$$

The direction of the angular momentum is perpendicular to the plane of the parent; i.e., j_{H_2} is perpendicular to $\mathbf{v}$ and to $\boldsymbol{\mu}$.

The impulsive model only gives a single value for j_{H_2} , $\omega'_{r'}$, and $\theta'_{r'}$. It does not account for a distribution of rotational states or angles. Parent rotation and vibration can transfer angular and linear momentum to the fragments. Because low J states of $H_2CO(S_1)$ are excited in this work, parent rotation is expected to transfer very little momentum to the products. Therefore, only the effect of parent vibrational motion on the product rotational distribution is considered here. The *ab initio* transition-state geometry and normal coordinates⁸ are used to describe the parent motions at the time of dissociation. The vibrations are treated quantum mechanically and are represented by harmonic oscillator wavefunctions. The phases of the five real modes are randomly selected, the Cartesian components of the linear momentum of each of the four atoms are determined, and the corresponding H_2 linear and angular momenta are classically calculated. The momenta from parent vibrational motion are added vectorially to the momenta from the impulsive force. The total fragment angular momentum is calculated and binned into the nearest quantum state. The angles between $\mathbf{v}$, $\mathbf{j}$, and $\boldsymbol{\mu}$ (the parent b axis) are evaluated and the bipolar moments are calculated using the semi-classical expressions listed in Eq. (6). These values are weighted by the probability of being in that part of phase space. This is repeated many (10^5 – 10^6) times until a suitable sampling of phase space has been accomplished.

The first set of calculations is performed using the same parameters that reproduced the rotational distributions in Ref. 7: zero-point vibrational excitation of the transition state with $x_{CO} = 0.27 \text{ \AA}$ and $x_{H_2} = 0.09 \text{ \AA}$ (corotating products). As a comparison, calculations are performed for $x_{H_2} = -0.09 \text{ \AA}$ (counterrotating products) and for $x_{H_2} = 0$. Note that the rotational distributions are reproduced reasonably well for all three sets of these parameters. Figure 8 compares the model results with the H_2 ($v=1$) vector correlations measured for $2^14^1 S_1 H_2CO$ photolysis; the model predicts vector correlations for H_2 ($v=3$) within 10% of the H_2 ($v=1$) correlations. In general, the agreement between this simple impulsive model and the measured correlations is poor. Changing the model parameters makes only modest differences in the magnitudes of the correlations.

The total energy in the 2^14^1 photolysis is about 1700 cm^{-1} above the barrier to dissociation.⁴⁵ This energy is large enough to excite 1 or 2 quanta of the two lowest fre-

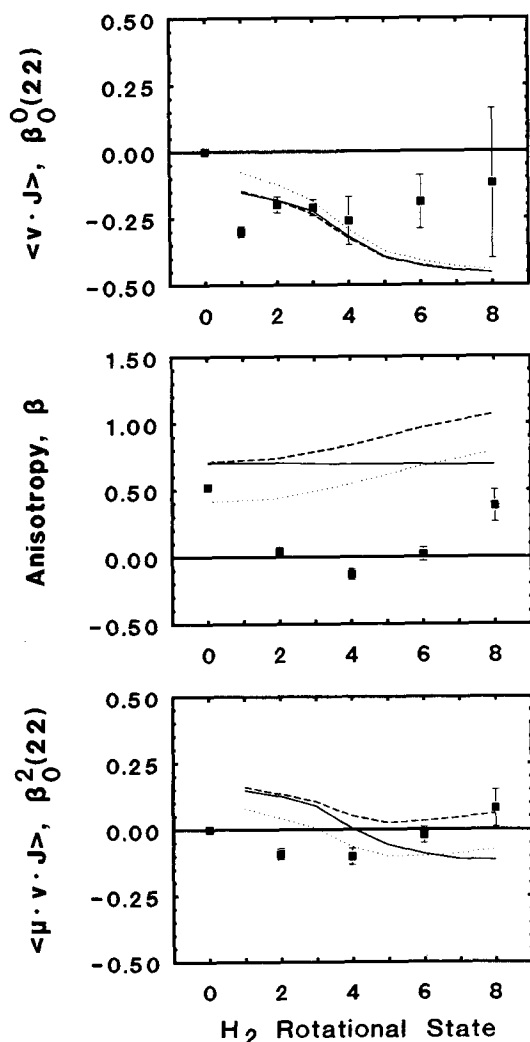


FIG. 8. The $H_2(v=1)$ impulsive model results with $E_{avl} = 30\,260 \text{ cm}^{-1}$ and $x_{CO} = 0.27 \text{ \AA}$. The dashed lines are the model results for $x_{H_2} = 0.06 \text{ \AA}$ (corotating products), the dotted lines for $x_{H_2} = -0.06 \text{ \AA}$ (counterrotating products), and the solid lines are for $x_{H_2} = 0$. The squares are the H_2 ($v=1$) vector correlations measured for $2^14^1 H_2CO$ photolysis.

quency modes of the transition state, ν_4 (the out-of-plane bend) and ν_5 (CH_2 wag). The model calculations are revised to include 1 or 2 quanta of excitation in these two modes. There are no major surprises. Increasing the out-of-plane bending excitation by one or two quanta produces a $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation with $\mathbf{v}$ less perpendicular to $\mathbf{J}$. This effect is more pronounced at low J than at high J [$\beta_0^0(22)$ increases by 0.19 for $J = 1$ and by 0.05 for $J = 8$ for 1 quantum of excitation in ν_4]. There is very little effect on the spatial anisotropy and the $\langle \mu \cdot \mathbf{v} \cdot \mathbf{J} \rangle$ correlation. One or two quanta of excitation in ν_5 makes less than a 5% difference in all three of the vector correlations.

When using the *ab initio* transition-state geometry, there are no model parameters (including modest excitation of harmonic transition-state modes) that can simultaneously fit the J_{CO} and J_{H_2} distributions (impact parameter ≈ 0.9 Å) and have a negative anisotropy as observed for all of the product H_2 from the $4^3 \text{ } ^1R_0(0)e$ photolysis. Within the scope of this model, either the transition dipole is different for the two photolyses, or the average geometry at the instant of dissociation is different.

The simple impulsive model reproduces the fragment rotational populations reasonably well, but not the vector correlations. From this, it appears that the details of the potential surface and/or the dynamics at the transition state play a more important role in determining fragment vector correlations than fragment rotational distributions.

IV. CONCLUSIONS

Several bipolar moments of the H_2 (ν, J) correlated angular momentum and velocity distribution produced from the photodissociation of formaldehyde have been measured by analysis of Doppler-resolved LIF line shapes. The values of $\beta_0^0(22)$ are negative and, within the error bars, constant as a function of H_2 (ν, J) and photolysis transition. It is determined that the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation is closer to the limit of $\mathbf{v} \perp \mathbf{J}$ than to $\mathbf{v} \parallel \mathbf{J}$. The many parent rotations prior to dissociation do not completely smear out the lab frame vector correlations. Anisotropy parameters as large as 0.85 and as small as -0.41 have been measured which are outside the limits imposed by classical models of parent rotation. A quantum mechanical model for parent rotation accounts for the large magnitude of the measured anisotropy parameters. Photolysis on the $^1R_0(0)$ line of the 4^3 band produces fragments with $\beta < 0$ while photolysis on the same rotational transition of the 2^14^1 band produces fragments with $\beta > 0$. It is not known if the different anisotropies are caused by differences in the parent transition dipole moment or by differences in the dissociation dynamics. The simple impulsive model that reproduces the fragment rotational distributions and product quantum-state correlations does not adequately describe the measured H_2 (ν, J) vector correlations.

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- ¹C. B. Moore and J. C. Weisshaar, *Ann. Rev. Phys. Chem.* **34**, 525 (1983).
- ²P. L. Houston and C. B. Moore, *J. Chem. Phys.* **65**, 757 (1976).
- ³D. J. Bamford, S. V. Filseth, M. F. Foltz, J. W. Hepburn, and C. B. Moore, *J. Chem. Phys.* **82**, 3032 (1985).
- ⁴M. Péalat, D. Debarre, J.-M. Marie, J.-P. E. Taran, A. Tramer, and C. B. Moore, *Chem. Phys. Lett.* **98**, 299 (1983).
- ⁵D. Debarre, M. Lefebvre, M. Péalat, J.-P. E. Taran, D. J. Bamford, and C. B. Moore, *J. Chem. Phys.* **83**, 4476 (1985).
- ⁶T. J. Butenhoff, K. L. Carleton, M.-C. Chuang, and C. B. Moore, *J. Chem. Soc., Faraday Trans. 2* **85**, 1155 (1989).
- ⁷T. J. Butenhoff, K. L. Carleton, and C. B. Moore, *J. Chem. Phys.* **92**, 377 (1990).
- ⁸J. D. Goddard and H. F. Schaefer, III, *J. Chem. Phys.* **70**, 5117 (1979).
- ⁹J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, III, *J. Chem. Phys.* **75**, 3459 (1981).
- ¹⁰G. E. Scuseria and H. F. Schaefer, III, *J. Chem. Phys.* **90**, 3629 (1989).
- ¹¹M. Dupuis, W. A. Lester, B. H. Lengsfeld, and B. Liu, *J. Chem. Phys.* **79**, 6167 (1983).
- ¹²M. J. Frisch, R. Krishnan, and J. A. Pople, *J. Phys. Chem.* **85**, 1467 (1981).
- ¹³P. Ho, D. J. Bamford, R. J. Buss, Y. T. Lee, and C. B. Moore, *J. Chem. Phys.* **76**, 3630 (1982).
- ¹⁴R. N. Dixon, *J. Chem. Phys.* **85**, 1866 (1986).
- ¹⁵P. L. Houston, *J. Phys. Chem.* **91**, 5388 (1987); G. E. Hall and P. L. Houston, *Annu. Rev. Phys. Chem.* **40**, 375 (1989).
- ¹⁶G. E. Hall, N. Sivakumar, P. L. Houston, and I. Burak, *Phys. Rev. Lett.* **56**, 1671 (1986).
- ¹⁷G. E. Hall, N. Sivakumar, D. Chawla, P. L. Houston, and I. Burak, *J. Chem. Phys.* **88**, 3682 (1988).
- ¹⁸The notation $2^1_04^3_0$ refers to absorption from the vibronic origin of S_0 ($\nu'_1, \dots, \nu'_6 = 0$) to the vibrational level having 1 quantum of ν_2 ($\nu'_2 = 1$) and 3 quanta of ν_4 ($\nu'_4 = 3$) in S_1 . Since all transitions in this work originate in the ground vibronic level, the subscript 0 is omitted.
- ¹⁹B. Schramm, D. J. Bamford, and C. B. Moore, *Chem. Phys. Lett.* **98**, 305 (1983).
- ²⁰The notation $^Q_{K_e}K_p(J'')$ denotes a $\Delta K_a = +1$, $\Delta J = 0$ transition in absorption from the $J''K''_a$ ground state. Symbols o and e indicate whether $J'' + K''_a + K''_c$ is odd or even. The rotational states are denoted $J_{K_aK_c}$, where K_a and K_c are the K quantum numbers of the state in the prolate and oblate symmetric top limits.
- ²¹K.-H. Gericke, S. Klee, F. J. Comes, and R. N. Dixon, *J. Chem. Phys.* **85**, 4463 (1986).
- ²² $P_2(x) = (1/2)(3x^2 - 1)$; $P_4(x) = (1/8)(35x^4 - 30x^2 + 3)$; $P_6(x) = (1/16)(231x^6 - 315x^4 + 105x^2 - 5)$.
- ²³C. H. Greene and R. N. Zare, *J. Chem. Phys.* **78**, 6741 (1983).
- ²⁴C. H. Greene and R. N. Zare, *Ann. Rev. Phys. Chem.* **33**, 119 (1982).
- ²⁵R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).
- ²⁶A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U.P., Princeton, NJ, 1957).
- ²⁷R. D. van Zee, T. J. Butenhoff, and C. B. Moore (unpublished results).
- ²⁸C. Jonah, *J. Chem. Phys.* **55**, 1915 (1971).
- ²⁹S. Yang and R. Bersohn, *J. Chem. Phys.* **61**, 4400 (1974).
- ³⁰The Euler angle convention described in Refs. 25 and 26 is used.
- ³¹W. H. Miller, *J. Am. Chem. Soc.* **101**, 6810 (1979).
- ³²W. F. Polik, D. R. Guyer, and C. B. Moore, *J. Chem. Phys.* **92**, 3453 (1990).
- ³³W. F. Polik, D. R. Guyer, W. H. Miller, and C. B. Moore, *J. Chem. Phys.* **92**, 3471 (1990).
- ³⁴W. E. Howard and E. W. Schlag, *J. Chem. Phys.* **68**, 2679 (1978).
- ³⁵W. E. Howard and E. W. Schlag, in *Radiationless Transitions*, edited by S. H. Lin (Academic, New York, 1980).

- ³⁶T. J. Butenhoff, Ph.D. dissertation, University of California (1990).
- ³⁷T. J. Butenhoff, K. L. Carleton, R. D. van Zee, and C. B. Moore (to be published).
- ³⁸D. A. Ramsay and S. M. Till, *Can. J. Phys.* **57**, 1224 (1979).
- ³⁹D. J. Clouthier and D. A. Ramsay, *Ann. Rev. Phys. Chem.* **34**, 31 (1983).
- ⁴⁰C. M. Kerr and D. A. Ramsay, *J. Mol. Spectrosc.* **87**, 575 (1981).
- ⁴¹C. M. Kerr, D. C. Moule, and D. A. Ramsay, *Can. J. Phys.* **61**, 6 (1983).
- ⁴²R. D. van Zee, T. J. Butenhoff, L. Geng, and C. B. Moore (unpublished results).
- ⁴³H. B. Levene and J. J. Valentini, *J. Chem. Phys.* **87**, 2594 (1987).
- ⁴⁴G. E. Busch and K. R. Wilson, *J. Chem. Phys.* **56**, 3626 (1972).
- ⁴⁵D. R. Guyer, W. F. Polik, and C. B. Moore, *J. Chem. Phys.* **84**, 6519 (1986).