Analysis and deconvolution of some $J' \neq 0$ rovibronic transitions in the high resolution $S_1 \leftarrow S_0$ fluorescence excitation spectrum of pyrazine[a]

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Fluorescence excitation spectra are reported for several $J' \neq 0$ rotational members of the 0_0^0 band of the $S_1(^1B_{3u}) \leftarrow S_0(^1A_{1g})$ electronic transition of pyrazine at a resolution of about 10 MHz. The transitions studied, namely $R(0)-R(2)$ and $P(2)-P(4)$, are each split into a large number of sharp lines ascribed, as in the case of the previously studied $P(1)$ ($J' = 0$) transition, to coupling with the lowest triplet state $T_1(^3B_{3u})$. Despite this complexity, we show in this paper that it is possible to separate the lines into clusters of transitions that terminate in the same K' component of the electronically excited, mixed S_1-T_1 state. This demonstrates that K' is a good quantum number, at least at low J' in the zero-order S_1 state. From this analysis, we determine the rotational constants of the S_0 and S_1 states. We also determine: (i) the relative cluster intensities; (ii) the coupled T_1 level densities; and (iii) by using standard deconvolution techniques, the S_1-T_1 coupling matrix elements, each as a function of J',K'. Cluster intensities decrease with increasing J', but $K' = 0$ clusters are significantly less intense than $K' \neq 0$ clusters in the fluorescence excitation spectra. Observed triplet level densities in each cluster exceed by an order of magnitude the calculated density of rovibronic states if selection rules appropriate to the D_{2h} point group are taken into account. Neither the observed level densities nor the coupling matrix elements (which vary from less than 5 MHz to more than 500 MHz) show a clear-cut systematic dependence on J' or K', although $K' = 0$ levels appear to be more strongly coupled than $K' \neq 0$ levels. Possible explanations for these results and their implications for intersystem crossing dynamics in the isolated molecule are discussed.

INTRODUCTION

The fluorescence decay behavior of pyrazine has frequently been considered typical of that of a molecule of intermediate size.[1,2] In small molecules, fluorescence tends to decay exponentially with unit quantum yield, as expected for excitation of a single Lorentzian line. In large molecules, the state reached by optical excitation is not a single molecular eigenstate, but a superposition of many of these states. Equivalently, this means that the bright zero-order state is coupled to a dense manifold of dark zero-order states. If this manifold is dense enough, it acts as a *quasi*continuum to which the energy is transferred irreversibly by a radiationless process. The fluorescence still decays exponentially, but with a quantum yield less than unity. For molecules of intermediate size, the manifold is not dense enough to be treated as a continuum, so that the fluorescence decay will generally be nonexponential.

In the case of pyrazine, Lahmani, *et al.*[1] observed biexponential decay. This has since been confirmed by more recent work[3–6] employing pulsed laser/supersonic jet techniques. Typically, $J' \neq 0$ rotational states accessed by selective excitation in the $S_1 \leftarrow S_0$ vibronic origin decay biex-

ponentially with rate constants of the order of 10^{10} and 10^7 s^{-1}. The $J' = 0$ level exhibits single exponential decay under nanosecond excitation conditions.[7] Quantum beats have been observed in time-resolved studies of other bands or of the 0_0^0 band under different excitation conditions.[8,9] All states exhibit low quantum yields, 0.05 or less.[10–12] Both the decay behavior and the quantum yield are strongly dependent upon the rotational state.

These results are understood qualitatively, but not quantitatively, despite careful study of their dependence on the rotational quantum number J'.[3–13] Obviously, the dynamics is dependent on the detailed level structure. Recently, it has been shown[14–16] that each rotational member of the 0_0^0 band exhibits a rich underlying structure of sharp lines. Since this structure and the corresponding decay patterns are influenced by magnetic fields,[2,5,7] it follows that the levels accessed in the $S_1 \leftarrow S_0$ transition also have triplet character. The structure can be described as resulting from singlet-triplet mixing, specifically S_1-T_1 mixing. (A higher-energy triplet state T_2 would have a very low level density near the S_1 origin and should contribute only incidentally or indirectly.) Thus, the radiationless process being monitored in these experiments is intersystem crossing (ISC).

The sharp lines observed in the high-resolution spectra have widths of order 10 MHz and are generally well separat-

ed in frequency, at least at low J', making possible lifetime studies of the mixed S_1-T_1 eigenstates. These[15] show, for $J' = 0$, that the mixed levels decay exponentially with rate constants of the order of 10^6-10^7 s^{-1}, corresponding to homogeneous widths of order 1 MHz or less. Since the observed widths in the frequency domain are larger than this, they must be inhomogeneous in nature; limited, e.g., by the Doppler effect. Still, even at 10 MHz resolution, pyrazine shows no intermediate-molecule behavior since the observed decays are exponential. Nonexponential decay is observed only when a group of lines in a rovibronic band is coherently excited.[16-19]

The relationship between the observed level structure and the time dependence of the fluorescence decay is further complicated by two factors. First, most observed spectra are excitation spectra rather than absorption spectra. It has been shown, for the $P(1)$ transition,[15] that the quantum yield varies considerably among the levels accessed in a single rovibronic band. If the same is true for other transitions, the two spectra will not be the same. Second, most bands contain contributions from states with different rotational quantum numbers K',[6] so that the corresponding spectra will be incoherent superpositions of spectra of different K' values. Before the singlet–triplet mixing can be analyzed, it is therefore necessary to separate contributions corresponding to the different K''s.

In this paper, we report high resolution excitation spectra of six $J' \neq 0$ rotational members [$R(0)$–$R(2)$ and $P(2)$–$P(4)$] of the 0_0^0 band of the $S_1(^1B_{3u}) \leftarrow S_0(^1A_{1g})$ electronic transition of pyrazine and propose a partial assignment. Earlier versions of a few of these spectra have been reported elsewhere.[2,16] To analyze these data, we note that pyrazine is an asymmetric top and start from the rotational constants derived from lower resolution spectra by Thakur and Innes (TI).[20] We use these constants for an initial prediction of the positions of the $J'K' \leftarrow J''K''$ rovibronic transitions. These positions are close to the centers of gravity of distinct clusters of lines in some of the spectra, thereby allowing a tentative assignment. Moreover, matching clusters can be recognized in $P(J'')$ and $R(J''\text{-}2)$ spectra corresponding to transitions to the same final states $J' = J'' \pm 1$. This recognition is greatly facilitated by the occurrence of characteristic groups of lines in the spectra. In the following sections, we then show that this leads to an effective separation of many of the K' components, thereby demonstrating that extensive K' mixing does not occur in the zero-order S_1 state at this level of resolution. We then subject each J',K' cluster to a standard rotational analysis, which yields inertial constants for the S_0 and S_1 states. We also determine from these data: (i) the relative cluster intensities; (ii) the T_1 level densities; and (iii) the S_1-T_1 coupling matrix elements, for each allowed J',K' value. The availability of these results then allows comment on the dynamics of the ISC process in pyrazine and its possible rotational state dependence.

RESULTS

A complete description of our experimental apparatus and procedures has been given elsewhere.[21] Briefly, we used a tunable cw laser operating in the ultraviolet as the excita-

tion source, and a molecular beam formed by expanding a mixture of pyrazine in argon as the absorber. Power normalized and calibrated fluorescence excitation spectra of selected rovibronic transitions in the 0_0^0 band of the $S_1 \leftarrow S_0$ spectrum of pyrazine were obtained by scanning the laser and detecting the undispersed emission using a photomultiplier tube and photon-counting system. Figures 1–3 illustrate the results obtained in zero-applied magnetic field[22] for six transitions: $R(0)$ and $P(2)$ (Fig. 1), $R(1)$ and $P(3)$ (Fig. 2), and $R(2)$ and $P(4)$ (Fig. 3), where the numbers in parentheses refer to the J value of the lower state (J''). Typical lines in these spectra exhibit widths of the order of 10 MHz, although even at this resolution some lines are incompletely resolved.[16] The analyses described below were performed on appropriately scaled and greatly magnified spectra generated using our PDP11-23/+ computer system, with which the experimental data were originally acquired.

ANALYSIS

Our analysis of these results assumes the standard rotational selection rules for a c-type band of a near oblate asymmetric top $\Delta J = 0, \pm 1$ and $\Delta K(K \equiv K_{+1}) = 0$. For practical reasons, we consider only the $\Delta J = \pm 1$ transitions, readily recognized as P and R branches. Each of these transitions consists of a superposition of all possible $\Delta K = 0$ transitions. The splitting of the different $\Delta K = 0$ transitions in
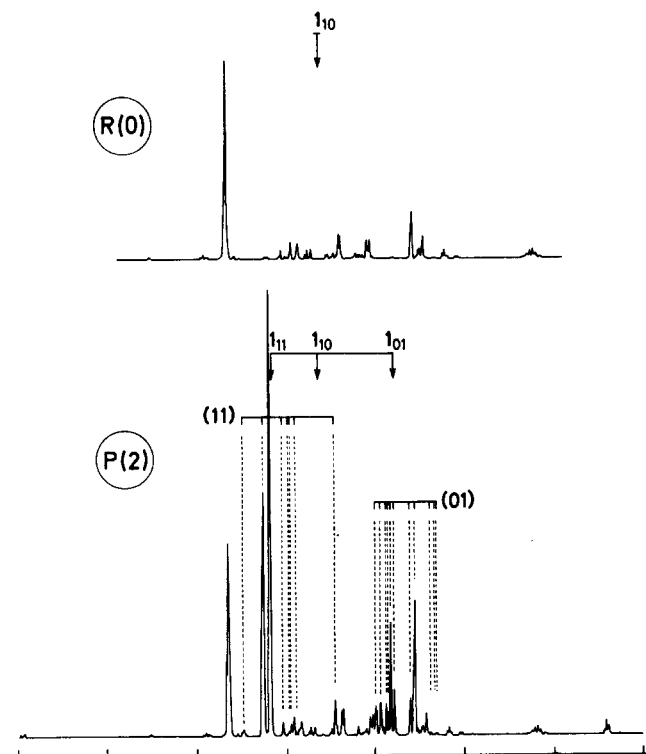

FIG. 1. High-resolution fluorescence excitation spectra of the $R(0)$ and $P(2)$ bands. Lines belonging to the two different $K = \pm 1$ are indicated with horizontal bars; the numbers represent (K_{-1},K_{+1}). All remaining lines belong to $K = 0$. Vertical arrows show the positions of the centers of gravity of the pure rovibronic transitions; the $J_{K_{-1},K_{+1}}$ quantum numbers of the upper S_1 level are indicated. Frequency is increasing from left to right. The frequency difference between the markers is 1 GHz.

each branch should increase with increasing J, approximately as $\frac{1}{2}(A - B)J(J + 1)$ for the $K = 1$ $[(K_{-1}, K_{+1}) = (J,1)$ and $(J - 1, 1)]$ levels. (Both the magnitude of this splitting and its dependence upon J is less for the $K > 1$ levels, for the J values considered here.) Thus, a comparison of the asymmetry splitting of different branches should make possible a determination of the rotational constant differences $(A - B)$ for both electronic states. Similarly, the separation of corresponding K components in different branches can be used to determine the rotational constant sums $(A' + B')$ and $(A'' + B'')$. All of this is well known to the practicing spectroscopist who often uses such a procedure for the determination of approximate inertial parameters. But what is interesting to us about this procedure is that its success or failure depends on whether or not the asymmetric rotor quantum numbers $K'_{-1} K'_{+1}$ are "good," and therefore on whether or not the eigenstates are extensively mixed with respect to K', at least at the present level of resolution. The existence of such mixing would signal an important (and as yet unconfirmed) role of rotations in the ISC dynamics.

We begin the analysis with a comparison of the $R(0)$ and $P(2)$ spectra, shown in Fig. 1. The $R(0)$ transition has, by ordinary selection rules, $(J',K') = (1,0) \leftarrow (J'',K'') = (0,0)$, and thus should consist of only a single line. But, like $P(1)$,[15] this transition exhibits several lines, owing to S_1–T_1 coupling. We can, however, easily determine the center-of-gravity (CG) of the distribution of oscillator strength in this cluster of lines. This is denoted as $J'_{K'_{-1}K'_{+1}} = 1_{10}$ in Fig. 1. Now, the $P(2)$ spectrum must contain all of the lines observed in $R(0)$, corresponding to $K = 0$, plus sets of additional lines belonging to $K = \pm 1$. The $K = 0$ components of $P(2)$ and their CG are thus readily identified by comparison of the two spectra. (The two spectra in Fig. 1 have been aligned so that the frequency positions 1_{10} coincide.) Then, the remaining lines in $P(2)$ must be assigned to either $K = +1$ or $K = -1$, since $(J',K') = (1,0) \leftarrow (J'',K'') = (2,0)$ and $(1, \pm 1) \leftarrow (2, \pm 1)$ for this transition. The $K = \pm 1$ lines cannot be separated immediately. However, if we assume that the rotational constants measured by TI[20] are approximately correct, then the experimental splitting should be equal to the separation of the CGs of the $K = \pm 1$ lines (1_{11} and 1_{01}) and roughly comparable to the splitting calculated from the TI[20] parameters. An assignment based on these assumptions is shown in Fig. 1. (The sign of K, $+$ or $-$, is assigned arbitrarily). This assignment requires that the two strongest lines in $P(2)$ have the same K value. The recent observation[23] of a quantum beat frequency corresponding to their separation is consistent with this conclusion. Also note from Fig. 1 that the $K = \pm 1$ clusters in $P(2)$ are well separated in frequency.

One further important assumption is made in this and the following interpretations. This is that the CGs determined from the fluorescence excitation spectra correspond, exactly, to the positions of the zero-order singlet levels from which the oscillator strength is derived. This need not be the case if, e.g., the levels accessed in a given cluster have significantly different quantum yields. To test this assumption, then, we can compare the excitation spectra with the recent-

ly obtained high-resolution absorption spectra.[24] Though these data are preliminary, this comparison shows that there are some important differences between the two. But there are important similarities, too. In particular, the relative intensities of the different lines in a given cluster appear to be essentially identical. Thus, we believe that the CGs determined from the excitation spectra are reliable enough measures of the zero-order singlet level positions to proceed with the analysis.

A corresponding comparison of the $R(1)$ and $P(3)$ bands is illustrated in Fig. 2. The $P(3)$ spectrum shows several clusters of lines. The expected large magnitude of the $K = \pm 1$ splitting suggests that the strong lines near the two band edges should be assigned to $K = +1$ and -1. Corresponding lines can easily be found in the $R(1)$ spectrum. The remaining lines in $R(1)$ must have $K = 0$; they have readily identifiable counterparts in $P(3)$. The lines in $P(3)$ without counterparts in $R(1)$ must then have $K = \pm 2$. This assign-
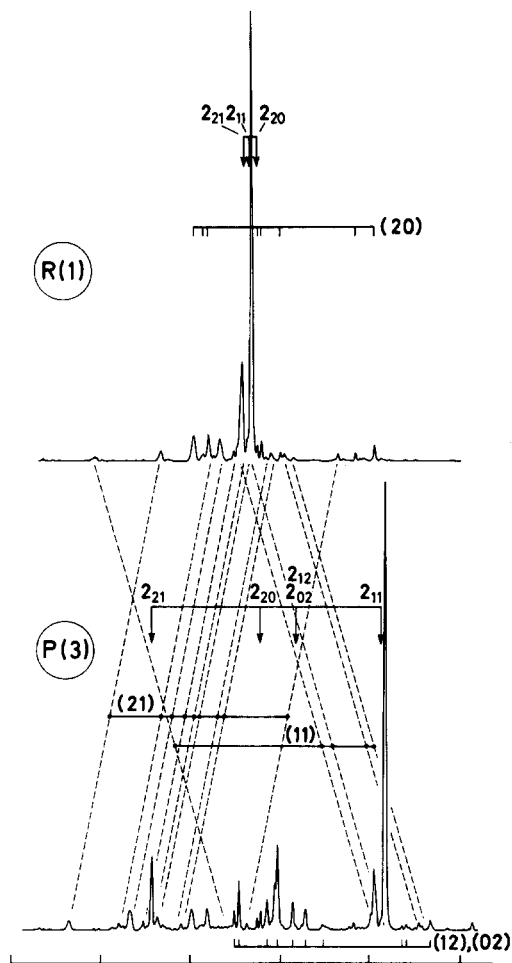

FIG. 2. High-resolution fluorescence excitation spectra of the $R(1)$ and $P(3)$ bands. Corresponding transitions to $K = \pm 1$ states are indicated with broken slanted lines and connected with horizontal solid lines and dots. Transitions to $K = \pm 2$ states are indicated with the bar below the $P(3)$ spectrum. The remaining transitions are to $K = 0$ and are lined up for the two spectra. The numbers within parentheses represent (K_{-1}, K_{+1}). The vertical arrows show the positions of the centers of gravity of the pure rotational transitions; the $J_{K_{-1},K_{+1}}$ quantum numbers of the upper S_1 levels are indicated. Frequency is increasing from left to right. The frequency difference between the markers is 1 GHz.

ment (see Fig. 2) accounts satisfactorily for all lines in the two spectra. It also makes possible an accurate measurement of $(A - B)$ in the ground state, since the difference in $K = \pm 1$ splitting between $P(3)$ and $R(1)$ is given by

$$\Delta(K = 1)_{P(J)} - \Delta(K = 1)_{R(J-2)}$$
$$= \tfrac{1}{2}(A'' - B'')J''(J'' + 1) - \tfrac{1}{2}(A' - B')J'(J' + 1)$$
$$\quad - [\tfrac{1}{2}(A'' - B'')(J'' - 1)(J'' - 2)$$
$$\quad - \tfrac{1}{2}(A' - B')J'(J' + 1)]$$
$$= \tfrac{1}{2}(A'' - B'')[J''(J'' + 1) - (J'' - 1)(J'' - 2)] \,.$$
$$\tag{1}$$

Thus, to determine $(A'' - B'')$, we superimposed the $R(1)$ and $P(3)$ spectra, aligned the $K' = 1$ clusters along the frequency axis, and then measured the shift of $R(1)$ relative to $P(3)$ that was required to achieve a $K' = -1$ cluster coincidence. The observed difference in $\Delta(K = 1)$ splitting is 2495 ± 15 MHz, yielding [from Eq. (1), with $J'' = 3$] $(A'' - B'') = 499 \pm 3$ MHz. This value may be compared with the TI value[20] of $(A'' - B'') = 456 \pm 6$ MHz determined from the absorption spectrum. Our procedure is accurate to within a typical linewidth in the high-resolution excitation spectrum. It also does not require knowledge of the exact CGs of the bands and so should be equally applicable to excitation and absorption spectra. For these reasons, we believe that our value of $(A'' - B'')$ is more reliable.

Unfortunately, we cannot also determine the excited state rotational constant difference $(A' - B')$ unambiguously from the present data since the equation

$$\Delta(K = 1)_{P(3)} - 6(\Delta K = 1)_{R(1)} = 15(A' - B') \,, \tag{2}$$

which can be transformed into

$$3(A' - B') = (A'' - B'') - \Delta(K = 1)_{R(1)} \tag{3}$$

requires knowledge of $\Delta(K = 1)_{R(1)}$, which is small. The observed splitting, based on the CGs of the $K = \pm 1$ components in the excitation spectrum, is 112 MHz, leading to $(A' - B') = 129$ MHz, compared to the value of 22 MHz obtained by TI.[20] In the absence of absorption or quantum yield data, it is difficult to estimate the reliability of our $(A' - B')$ value. We note, however, that for $P(2)$ our values of $(A'' - B'')$ and $(A' - B')$ lead to essentially the same $K = \pm 1$ splitting as the TI values[20] (1368 vs 1330 MHz), so that the present analysis of $P(2)$ remains valid.

A corresponding comparison of the $R(2)$ and $P(4)$ bands is illustrated in Fig. 3. The calculated $K = \pm 1$ splittings in $R(2)$ and $P(4)$ are 723(1236) and 4216(4428) MHz, respectively, the numbers in parentheses being based on the TI rotational constants.[20] The magnitudes of these splittings for $P(4)$ suggest that the strong bands at the two edges of this spectrum should again be attributed to the $K = +1$ and -1 components. The assignment is more complicated for the $R(2)$ spectrum because of its compactness resulting from the small K splitting. However, it is possible to find reasonably convincing clusters of $K = +1$ and -1 lines as counterparts of the clusters in the $P(4)$ spectrum which allows us to calculate $(A'' - B'')$ from Eq. (1). The result is

$$\Delta(K = 1)_{P(4)} - \Delta(K = 1)_{R(2)} = 7(A'' - B'')$$
$$= (3444 \pm 20) \text{ MHz}, \tag{4}$$

or $(A'' - B'') = (492 \pm 3)$ MHz, in good agreement with the results from $R(1)$ and $P(3)$. To estimate $(A' - B')$ from $R(2)$ and $P(4)$, we use the relation

$$3\Delta(K = 1)_{P(4)} - 10\Delta(K = 1)_{R(2)} = 42(A' - B') \tag{5}$$

which can be transformed into

$$6(A' - B') = 3(A'' - B'') - \Delta(K = 1)_{R(2)} \,. \tag{6}$$

Unfortunately, $\Delta(K = 1)_{R(2)}$ cannot be determined accurately, since both the $R(2)$ and $P(4)$ spectra are very crowded and not all lines have been assigned. Our present best estimate $\Delta(K = 1)_{R(2)} = 1610$ MHz leads to $(A' - B') = -20$ MHz, compared to the result $(A' - B') = 129$ MHz derived from Eq. (3). If valid, the latter result would imply $\Delta(K = 1)_{R(2)} = 900$ MHz.

Despite these numerical difficulties, we claim on the basis of the above arguments that it is possible to assign, by traditional spectroscopic methods, the complex $J' \neq 0$ spectra of pyrazine in terms of the asymmetric rotor quantum numbers $K'_{-1}K'_{+1}$ of the zero-order S_1 state. From this result, we conclude that K' (i.e., $K'_{-1}K'_{+1}$) is a good quan-
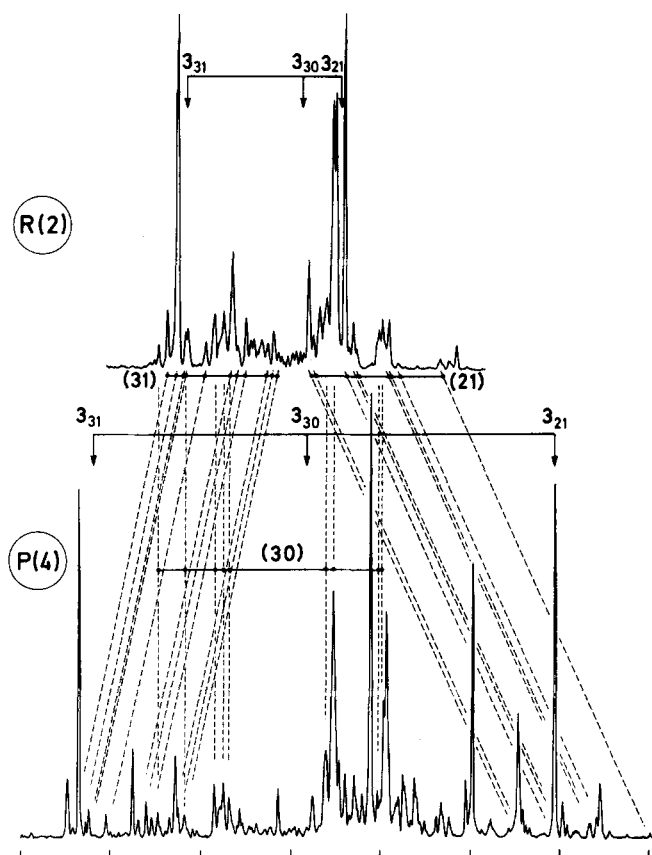

FIG. 3. High-resolution fluorescence excitation spectra of the $R(2)$ and $P(4)$ bands. Corresponding transitions to $K = \pm 1$ and 0 states are indicated with broken slanted lines and connected horizontal solid bars and dots for $K = \pm 1$. The transitions to $K = 0$ are lined up in the two spectra. Numbers within parentheses represent (K_{-1}, K_{+1}). The remaining transitions in $P(4)$ belong to $K = \pm 2$ and ± 3. Vertical arrows show the positions of the centers of the gravity of the pure rotational transitions; the $J_{K_{-1}, K_{+1}}$ quantum numbers of the upper S_1 levels are indicated. Frequency is increasing from left to right. The frequency difference between the markers is 1 GHz.

TABLE I. Observed and calculated rovibronic frequencies in the 0_0^0 band of the $^1B_{3u} \leftarrow {}^1A_{1g}$ transition of pyrazine. Frequencies are in MHz relative to the band origin ν_0.

Transition	$(J', K'_{-1} K'_{+1})$	Observed value	Estimated error	(Observed–calculated) Fit I	Fit II
P4	(3,3,0)	− 50 100	75	− 20	188
	(3,3,1)	− 52 342[a]	75	− 830	− 298
	(3,2,1)	− 47 288	75	− 7	− 12
P3	(2,2,0)	− 37 138	75	95	113
	(2,2,1)	− 38 322	75	− 40	143
	(2,1,1)	− 35 711	75	− 56	− 123
	(2,1,2) (2,0,2)	− 36 726[b]	75	33	177
P2	(1,1,0)	− 24 798	75	− 107	− 220
	(1,1,1)	− 25 293	75	16	− 35
	(1,0,1)	− 23 890	75	45	− 71
P1[c]	(0,0,0)	− 12 203	75	114	294
R 0	(1,1,0)	12 216	75	− 104	− 232
R 1	(2,2,0)	24 742	75	96	102
	(2,2,1)	24 544	75	− 38	159
	(2,1,1)	24 656	75	− 65	− 208
R 2	(3,3,0)	36 940	75	14	229
	(3,3,1)	35 785[a]	75	− 807	− 248
	(3,2,1)	37 395	75	27	− 75

[a] Omitted from the least-squares fit I (see the text).
[b] These two transitions could not be separated in the experimental spectrum. The calculated pure rotational splitting is 292 MHz.
[c] Reference 15.

tum number in the S_1 zero-point vibrational level, at least at 10 MHz resolution.

Rotational constants

So far, we have only considered splittings within a given P or R band, which demonstrate the goodness of K' and yield approximate values of the rotational constant differences $(A − B)$. But the separation of the corresponding K components in different bands can be used to determine the rotational constant sums $(A + B)$. Combining these results then, we can determine the inertial parameters of both electronic states. The absolute accuracy of this determination is limited by: (i) the accuracy with which the CGs of these components can be determined from the excitation spectra, and (ii) the possible differences between these CGs and the singlet components corresponding to the CGs of the absorption spectra. The (approximate) CG of an absorption spectrum is available only for $P(1)$.[15] It is listed in Table I, along with the CGs of the excitation spectra of the different $J' \neq 0$ rotational bands determined in this work (relative to the estimated band origin ν_0), together with the estimated errors of these measurements.

We now use these CGs to obtain an overall fit to the Hamiltonian of the asymmetric rigid rotor following standard procedures. The parameters determined in this calculation are A'', B'', A', B', C', with C'' fixed by the planarity relation $(1/C'') = (1/A'' + 1/B'')$. Reported in Table I are the results of two different least-squares fits of this type, labeled I and II. Fit I omits two CGs, namely those for transitions terminating in the zero-order $J'_{K'_{-1} K'_{+1}} = 3_{31}$ state. Fit II includes all CGs. Examining the two fits, we see that fit I is more satisfactory, as judged by comparing the included (ob-

served–calculated) frequency differences to the estimated errors.

We can also test the quality of the two fits by comparing how well they reproduce the accurately known frequency difference $(A'' − B'')$. Table II lists the two sets of rotational constants determined in this work, together with those of TI.[20] Set I gives $(A'' − B'') = 498$ MHz and set II gives $(A'' − B'') = 480$ MHz. Comparing these two values to the experimental value of 496 ± 3 MHz leads again to the conclusion that fit I is superior. Also, fit I gives a value of C' much closer to that appropriate for a planar molecule, in agreement with expectations for the zero-point vibrational level of the S_1 state. We therefore favor fit I, and tentatively ascribe the discrepancy observed for the 3_{31} state to missing

TABLE II. Rotational constants (in MHz) of pyrazine in the $S_0 ({}^1A_{1g})$ and $S_1 ({}^1B_{3u})$ states.[a]

Constant	Thakur and Innes[b]	Set I[c]	Set II[c]
A''	6386(3)	6407 (10)	6402 (22)
B''	5930(3)	5909 (10)	5922 (27)
C''	3075(1)	3074[d]	3076[d]
A'	6108(6)	6219 (15)	6129 (40)
B'	6086(6)	6099 (15)	6129 (40)
C'	3050(1)	3085[e] (20)	3027[e] (60)

[a] $\nu_0 = 30\,875.777$ (10) cm^{-1}.
[b] Reference 20.
[c] $(A'' − B'') = 498$ MHz (set I) or 480 MHz (set II) compared to the value (496 ± 3) MHz obtained from the differences in the $P(J)$ and $R(J − 2)$ splittings measured experimentally.
[d] Calculated from the planarity relation.
[e] The planarity relation yields 3079 MHz (set I) and 3064 MHz (set II).

and/or overlooked $K = \pm 1$ lines in the crowded $R(2)$ and $P(4)$ spectra.

Relative cluster intensities

We now examine other properties of these spectra that may be of dynamical interest. One of these properties is the total integrated relative intensity, in fluorescence excitation, of one J',K' cluster compared to another, I_{rel}. To make this comparison quantitative, we arbitrarily assigned the value $I_{\text{rel}} = 100$ to the sum of the integrated intensities of all lines in the $P1$ transition. We then measured the total integrated intensity of all lines belonging to each J',K' cluster, compared that value to the corresponding value for the $P1$ transition (or other reference cluster) under identical experimental conditions, and assigned each J',K' cluster an appropriate intensity. These intensities were then corrected for differences in nuclear spin statistical weights, Hönl–London factors, and Boltzmann factors to determine the I_{rel} values. Given this procedure, the I_{rel} values are measures of the relative brightness of different clusters, and so should all be equal to 100 if all J',K' clusters have the same quantum yield. The observed values, estimated to be accurate to $\pm 10\%$, are listed in Table III.

Examination of these results reveals some interesting trends. First, we find that I_{rel} decreases monotonically with increasing J'. Averaging over the different possible K' yields values of $I_{\text{rel}} = 100$, 73, and 32 for $J' = 0$, 1, and 2. (Not all K''s were measured for $J' = 3$.) This trend is consistent with earlier low-resolution quantum yield measurements[10–12] that show a systematic decrease in the relative intensities of the different rovibronic transitions in the $S_1 \leftarrow S_0$ excitation spectrum with increasing J'. Second, we find, averaging over

TABLE III. Relative cluster intensities, number and density of triplet states, and singlet–triplet coupling parameters (in MHz) derived from the high-resolution fluorescence excitation spectra of pyrazine, as a function of the asymmetric rotor quantum numbers of the zero-order S_1 state.

J'	K'_{-1}	K'_{+1}	$I_{\text{rel}}{}^a$	N	$\rho = N/\text{cm}^{-1}$	V_{max}	V_{rms}
0	0	0	100	47	276	441[b]	106[b]
1	1	0	32	100	647	460	106
1	1	1	131	13	408	145	47
1	0	1	57	48	560	128	38
2	2	0	16	29	233	525	169
2	2	1	14	10	167	160	109
2	1	1	64	10	144	220	78
2	1	2	64[c]	29[c]	253[c]	249[d]	127[d]
2	0	2					
3	3	0	15	14	177	588	187
3	3	1	53	11	291	277	116
3	2	1	32	10	185	172	91

[a] Corrected (see the text) integrated intensity of each $J'_{K'_{-1}K'_{+1}}$ cluster, relative to an assumed value of 100 for $J'_{K'_{-1}K'_{+1}} = 0_{00}$. The estimated uncertainty in these values is $\pm 10\%$.

[b] From the excitation spectrum. The corresponding couplings derived from the absorption spectrum of $P(1)$ are $V_{\text{max}} = 479$ MHz and $V_{\text{rms}} = 206$ MHz (Ref. 15).

[c] To make these values crudely comparable with the others in the table they should be divided by two.

[d] The actual couplings are smaller; the two $|K| = 2$ components are separated by about 290 MHz.

the different possible J' values, that the values of I_{rel} for different K' are approximately the same ($I_{\text{rel}} = 41$, 59, and 32 for $K' = 0$, 1, and 2). This comparison is of limited value since we access only two states with $K' > 1$. But, third, we find that the relative intensities of $J' \neq 0$, $K' = 0$ clusters are significantly less than those for $J' \neq 0$, $K' \neq 0$ clusters. Table III shows that I_{rel} for $K' = 0$ levels is typically a factor of 3 smaller than the average I_{rel} values for $K' \neq 0$ levels belonging to a particular J'.

Densities of states

Next, we determine the approximate density of interacting triplet levels for each J',K' rotational state. We count the number of lines that appear in each cluster and divide that number by the frequency width spanned by each cluster. The results are also listed in Table III. The average number of levels per state per cm^{-1} is 278. (This is probably an underestimate since, especially for $J' = 2$ and 3, line coincidences likely occur.) All J',K' state densities are of the same order of magnitude, although large deviations from the average value do occur. Given the difficulties of the assignment of specific transitions to individual states, and of the measurement of exact frequency intervals, we do not regard these fluctuations as significant. We therefore conclude that each individual J',K' S_1 rovibronic level interacts with approximately the same number of background triplet rovibronic levels near the origin of the $S_1 \leftarrow S_0$ transition.

The calculated density of vibrational levels for an S_1–T_1 interval[25] of 4056 cm^{-1}, based on the Haarhoff equation,[26] is 140 per cm^{-1}, an estimate confirmed by direct level counting. This is probably also an underestimate, since in the calculations we used ground-state frequencies[27] for modes for which no T_1[28–30] or S_1[31] frequencies are available and ignored anharmonicity. Since ground-state frequencies tend to be higher, the resulting calculated density is expected to be low. The value of 140 per cm^{-1} leads, after multiplication by the spin multiplicity ($= 3$) and division by the number of irreducible representations of the D_{2h} point group ($= 8$),[32] to a calculated density of 53 levels per cm^{-1} (106/cm^{-1} if the symmetry is D_2, which seems unlikely). In view of the relatively large zero-field splittings in pyrazine (10 142 and 424 MHz in the condensed phase),[33] at least one of the triplet components is likely to be offscale in each of the spectra reported here, so that the effective spin multiplicity is not three, but one or two. This leads to a calculated triplet level density of 18–35 per cm^{-1} in D_{2h} (35–70/cm^{-1} in D_2), approximately an order of magnitude smaller than the observed density.

Singlet–triplet couplings

Finally, we use the Lawrance–Knight procedure[34] to deconvolute each of the J',K' clusters into zero-order states and the set of couplings for each J',K' singlet component and the triplet levels with which it is mixed. Strictly speaking, this procedure is again valid only for absorption spectra. However, as noted earlier, the observed excitation spectra broadly resemble the corresponding absorption spectra as measured recently under low signal-to-noise conditions.[24]

Therefore, applying this procedure to the excitation spectra should have at least qualitative significance.

The derived couplings range from less than 5 MHz to greater than 500 MHz. Since the lower range of coupling strengths is likely to be limited by our ability to observe weak lines in these crowded spectra, we list in Table III the maximum coupling V_{max} along with the root-mean-square (rms) value V_{rms} of all the couplings for a given J',K' combination. For $J' = K' = 0$, we give, as well, the values appropriate to the absorption spectrum as reconstructed on the basis of the lifetimes and quantum yields of the strongest lines.[15] Comparison of all of these values shows that both V_{max} and V_{rms} are somewhat larger for $K' = 0$ levels. However, there is no other systematic dependence of these quantities on J',K'.

DISCUSSION

Dynamically, the most interesting results of our analysis of the six different $J' \neq 0$ rovibronic bands of the $S_1 \leftarrow S_0$ transition of pyrazine, accessing $J' = 1, 2$, and 3 of the zero-point vibrational level, are that (i) the asymmetric rotor quantum numbers $K'_{-1} K'_{+1}$ of the zero-order S_1 state are "good" quantum numbers at low J'; (ii) the observed average zero-order triplet level density is approximately an order of magnitude higher than that calculated using the appropriately modified Haarhoff formula; and (iii) neither the level densities nor the coupling matrix elements show any systematic dependence on J',K', although $K' = 0$ levels have somewhat larger values of V_{rms}. We also find that (iv) cluster intensities decrease with increasing J', but that (v) $K' = 0$ clusters exhibit lower intensity than $K' \neq 0$ clusters in the fluorescence excitation spectra.

The finding that $K'_{-1} K'_{+1}$ are good quantum numbers shows that both the direct coupling of the S_1 vibronic levels and the indirect coupling of these levels via the triplet (or other dark) manifold are negligible. Recall that, in the zero-order picture, a single bright S_1 level is mixed with a number of dark T_1 levels, resulting in a distribution of the oscillator strength over a number of molecular eigenstates. These are the states that are observed in the high resolution experiments. In our analysis of these results, we dediagonalize these states, refocusing the oscillator strength back into single CGs whose frequency positions are dictated by the positions and intensities of the lines in the eigenstate spectra. As long as the excitation and absorption spectra of a single cluster are exactly the same, and providing that we succeed in collecting all of the oscillator strength associated with a given initial state, we can expect the CG positions to correspond, exactly, to the frequency positions of the zero-order S_1 levels, before the S_1–T_1 coupling is turned on. This procedure assumes, of course, that there is no other coupling between these levels, either direct or indirect; i.e., that only a single zero-order S_1 level contributes oscillator strength to a given cluster. Our fitting procedure provides a stringent test of this assumption. And the fact that we can fit the CG positions derived from our analysis to the Hamiltonian of an asymmetric top, without additional coupling terms, shows that such coupling, if it exists, must be very small.

This is not a surprising result. That the direct coupling of S_1 rovibronic levels does not occur is reasonable since the levels are zero-point vibrational levels, not subject to Coriolis or centrifugal forces. The indirect coupling of these levels is also severely restricted by symmetry. The rotational eigenfunctions of a D_{2h} molecule must transform as A_g, B_{1g}, B_{2g}, or B_{3g}. This creates four symmetry-distinguishable manifolds that cannot interact because of the Pauli principle. These are $(J'_{K'_{-1}K'_{+1}})$

$$A_g: 0_{00}, 2_{20}, 2_{02}, 3_{22}, \ldots, \quad B_{1g}: 1_{11}, 2_{11}, 3_{31}, 3_{13}, \ldots,$$
$$B_{2g}: 1_{01}, 2_{21}, 3_{21}, 3_{03}, \ldots, \quad B_{3g}: 1_{10}, 2_{12}, 3_{30}, 3_{12}, \ldots.$$

Levels with the same symmetry can, of course, interact. But these interactions are further restricted by the selection rules $\Delta J_{ST} = 0$, $\Delta K_{ST} = 0, \pm 1$ and $\Delta J_{ST} = 0$, $\Delta K_{ST} = 0, \pm 2$ for vibronically and rotationally induced spin–orbit coupling, respectively. Thus, all K levels with $J = 0$ and 1 cannot mix. In fact, of all the levels considered in this paper, only the following pairs can interact: 2_{20} and 2_{02}, 3_{31} and 3_{13}, 3_{21} and 3_{03}, and 3_{30} and 3_{12}. Either spin–orbit mechanism is in principle capable of providing an indirect coupling route for these pairs. Moreover, Coriolis and/or other nonrigid-body couplings between the high-energy rovibronic levels of the triplet manifold can give rise to intermediate states of mixed K' character. But the zero-order frequency separations of all potentially interacting pairs, which all have $\Delta K_{+1} = 2$, are large ($\geqslant 12$ GHz) compared to the V_{rms} values, so no large shifts are expected. And, with the single possible exception of the 3_{31} state, none are found.

It is important to note that our results for the relative cluster intensities, level densities, and S–T coupling matrix elements are independent of any assumptions about the selection rules for ISC. We also obtain no information about the "goodness" of K' in the zero-order triplet state. The triplet rovibronic levels lying some 4000 cm^{-1} above the T_1 origin may, or may not, have well-defined asymmetric rotor quantum numbers. Other types of experiments will be necessary to determine whether these levels (and those of the ground state) are significantly mixed with respect to K'.

One possible explanation for the large difference in the observed and calculated average triplet level densities is that hyperfine splitting (hfs) due to coupling of the electron spins with the nuclear spins is actually resolved in the optical spectra. Ordinary pyrazine has two ^{14}N nuclei ($I = 1$) and four ^{1}H nuclei ($I = \frac{1}{2}$), leading to 144 possible nuclear spin states per (electron spin) rovibronic level. Many of these will, of course, be degenerate in zero external magnetic field and/or have the wrong symmetry to couple to the zero-order singlet state. But the hfs observed in the cation[35] and anion[36] radicals of pyrazine in solution is of the order of 20–50 MHz for the protons as well as for the ^{14}N nuclei. Comparable splittings may be expected for the zero-order ($J \neq 0$) triplet state,[37] in the gas phase at zero field. (Pyrazine also has a nonzero ^{14}N quadrupole coupling, but this is expected to be small.[38]) The total number of hyperfine-split lines with separations greater than 10 MHz in the optical spectrum of the mixed S_1–T_1 state will depend on the triplet character of the eigenstates, on their fine-structure parameters, and on their rotational quantum numbers. But, since the average triplet character of the states accessed in our experiment is high, it

would appear that a tenfold increase in the level density could be explained by hyperfine effects.

This interpretation may also account for the remarkable grouping of lines that is seen throughout the spectra and that greatly facilitates the recognition of the components of individual K' clusters. The figures show many characteristic examples. For instance, on the high-frequency side of Fig. 1, a group of 12 (1_{10}) lines appears in $R(0)$ and $P(2)$ with an average spacing of about 20 MHz, separated by more than 500 MHz from other 1_{10} lines. These smaller spacings could be hfs. Many other similar groups of lines can be easily recognized in all three figures.

Three other explanations for the difference in level densities occur to us. One is that $\Delta K \neq 0$ transitions also contribute to the spectra. However, a quantitative calculation of the expected intensities of these forbidden lines shows that they are far too weak to be observed under our experimental conditions. The second possibility is that isotopically labeled molecules are contributing to the spectra. The vertical dynamic range of our experiment is high enough to observe the lines from, e.g., a singly ^{13}C-substituted (natural abundance $\sim 4\%$) pyrazine. But, because of differences in zero-point vibrational energies, no lines of this type are expected near the $P(1)-P(4)$ and $R(0)-R(2)$ transitions of the unsubstituted molecule.[39] Third, there is also the possibility that ground state rovibronic levels are contributing to the spectra. The density of such levels near the S_1 origin is very high, at least 10^8 per cm^{-1}. If there is a small coupling between these levels and the mixed S_1-T_1 levels possessing oscillator strength, additional very closely spaced lines might appear under high resolution conditions.

We can only speculate about whether or not this is a reasonable explanation, but it is not an an unprecedented suggestion. In a recent high resolution study of the 0^0_0 band of the perturbed $S_1 \leftarrow S_0$ transition of pyrimidine,[40] it was found that the average lifetimes of selected levels with the same K'_{+1} and different J' increase approximately linearly with K'_{+1}. But the measured lifetimes of all levels are longer than the reciprocal spectral resolution, suggesting the existence of additional unresolved couplings. It was also found that the observed magnetic field effects on the spectra of pyrimidine could best be explained by postulating the existence of a coupling with a dense manifold of background levels, perhaps those of the ground state. A similar phenomenon could explain the enhanced level densities in the corresponding band in pyrazine, but only if the coupling is very restricted. If all, or nearly all ground state levels are involved then, because of their high density, they will behave as a continuum with respect to the S_1 state. This will only contribute width to the observed spectral lines, not additional structure.

The S_1-T_1 gap in pyrimidine is only half that of pyrazine, resulting in a much lower density of T_1 vibrational levels near the origin. As a result, pyrimidine's $S_1 \leftarrow S_0$ spectrum is much simpler and can be deperturbed in a straightforward manner. The analysis shows,[40] again using the Lawrance–Knight procedure,[34] that there is no pronounced J',K' dependence of the triplet level densities or coupling matrix elements for $J' \neq 0$ states.

The present results for pyrazine (Table III) are similar to those for pyrimidine. Neither the densities nor the maximum or rms couplings show a strong, systematic dependence on J' or K'. The frequency-resolved pyrazine mixed S_1-T_1 levels with $J',K' \neq 0$ appear to show, qualitatively, the same properties as those with $J',K' = 0$. If there are differences, they are quantitative. Thus, zero-order $K' = 0$ levels appear to exhibit larger coupling matrix elements V_{rms} than $K' \neq 0$ levels; $K' = 0$ clusters also exhibit lower intensities I_{rel} than $K' \neq 0$ clusters in the excitation spectra. If radiationless triplet (or ground state) decay following ISC is the dominant fluorescence quenching mechanism, then I_{rel} should vary quadratically with V_{rms}. The data in Table III appear consistent with this interpretation. So, also, are the available high-resolution absorption spectra,[24] which tend to show enhanced relative intensities for $K' = 0$ clusters compared to the corresponding clusters in the excitation spectra.

The second-order spin–orbit matrix elements describing the $^1B_{3u}-^3B_{3u}$ coupling, derived by Stevens and Brand,[41] offer no obvious explanation why a maximum in the coupling should be reached for $K' = 0$. On the contrary, they suggest that the effective coupling should increase with K' due to the opening of additional coupling channels. One may therefore expect that triplet levels with $|K'| \geqslant 1$ would be more strongly coupled than those with $K' = 0$ if only the spin–orbit interaction is important. However, this is contradicted by the present results, which tend to show larger V_{rms} and smaller I_{rel} values for $K' = 0$. If these trends, although small, are real and can be substantiated by additional measurements, then the only conclusion that one can reach is that other K'-dependent interactions are important in the ISC dynamics. It has been shown that the effect of such couplings, if they exist, is already contained in the matrix elements derived from the deconvolution procedure.[40] And since the measured values of V_{rms} (I_{rel}) are apparently larger (smaller) for $K' = 0$ than for $K' \neq 0$, perpendicular-type Coriolis coupling[42] is a logical source of these effects. But the present data are neither numerous enough nor precise enough to resolve these apparent ambiguities.

More serious difficulties arise on comparison of the present results with those obtained using lower resolution and/or time-domain methods. For example, it has been shown that, whereas the $J' = 0$ levels of the collision-free molecule exhibit single exponential decay following excitation with a few nanosecond laser pulse, the fluorescence decay of $J' \neq 0$ levels is biexponential with A^+/A^- values that increase approximately linearly with J', at low J'.[3,4,6] (High J' experiments, especially in the P branch, suffer from overlap of adjacent transitions, and so are more difficult to analyze). The linear dependence of A^+/A^- on J' has been interpreted as being due to a parallel-type Coriolis-induced mixing of the zero-order triplet and/or ground state levels, leading to K' scrambling.[7,43] As already noted, the present experiments can neither prove nor disprove this hypothesis. But, since A^+/A^- is, in the theory of the intermediate case,[1] proportional to the number of coupled states, this hypothesis also requires that there be an approximately linear increase in the value of the level density with increasing J', averaged over the different possible K'. We observe no such trend (Ta-

ble III). And the excitation spectra show no evidence of "grass," i.e., large numbers of weak lines or a continuous background at frequencies between the strong clusters of lines.[44]

As noted by de Lange, et al.,[19] it may well be that the dependence of A^+/A^- upon J' is totally determined by changes in the quantum yield rather than in the number of coupled states, since the nonradiative lifetime is much longer than the dephasing time. Indeed, we do find a monotonic decrease in I_{rel} values with increasing J', a result that is consistent with earlier quantum yield measurements,[10-12] as already noted. Still, we have no unambiguous explanation for this behavior. So the source of the rotational state dependence of the ISC dynamics in the isolated molecule remains an enigma.

ACKNOWLEDGMENTS

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