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Electronic relaxation of $^1B_{3u}(n\pi^*)$ pyrazine in a supersonic jet: Rotational state dependence of the nonradiative rate leading to biexponential decay

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COMMUNICATIONS

Electronic relaxation of $^1B_{3u}(n\pi^*)$ pyrazine in a supersonic jet: Rotational state dependence of the nonradiative rate leading to biexponential decay

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The effect of rotations on the lifetimes of molecules in their electronically excited states has recently become a subject of considerable interest. In formaldehyde the nonradiative rate seems to rather erratically increase with K,[1] in naphthalene the variation is very small,[2] and in glyoxal the collision cross section appears not to depend on the rotational state.[3] In this letter, we report the observation of a strong K^2 dependence of the nonradiative rate for the decay of the vibrationless first excited singlet state of pyrazine under collision-free conditions.

Our experiments were performed by monitoring the excitation wavelength and/or time dependence of the total fluorescence intensity of pyrazine which was expanded in a pulsed supersonic jet[4] of helium and excited with a frequency-doubled and narrowed dye laser pulse (bandwidth = 0.2 cm⁻¹, pulse duration = 10 nsec). Under these conditions, all $\Delta K = 0$ transitions originating in a particular J'' of the parallel-type bands lie within the laser linewidth. Figure 1 shows the excitation spectrum of the $^1B_{3u} \leftarrow {}^1A_g(0, 0)$ band. Depending on nozzle conditions, the rotational structure could be resolved up to $J' = 20$. Decay time measurements were performed from $J' = 2$ to $J' = 12$ using a boxcar integrator. Typical results are given in Fig. 2. For $J' = 2$, we find a single exponential decay of about 400 nsec. However, at higher J', a fast component appears whose relative contribution increases with increasing J'. The lifetime of the fast component is also strongly dependent on rotational state. Similar behavior is exhibited by single rotational levels belonging to the totally symmetric ν_{6a} vibronic band. Collisions were ruled out as being primarily responsible for these effects by the observation that the fast and slow components persist up to 6 cm downstream of the nozzle. At this distance, a 20 nsec decay would require a collision diameter greater than 10^4 Å².

Baba *et al.*[5] have recently shown that there is a marked variation in the fluorescence quantum yield of pyrazine across the rotational contour of the (0, 0) band, with ϕ_f peaking at low J'. Therefore, we believe that

the appearance of the fast component is associated with the increasing importance of a nonradiative channel at high J'. In the analysis of our data, we have found that the decay behavior can be fit by an expression of the form

$$I(J) = I_0 \sum_{K=-J}^{J} g_{JK} \frac{(J+1)^2 - K^2}{J+1}$$

$$\times \exp\{[- BJ(J+1) + \tfrac{1}{2}BK^2]/kT\} \exp[-(aK^2 + f)t] , \quad (1)$$
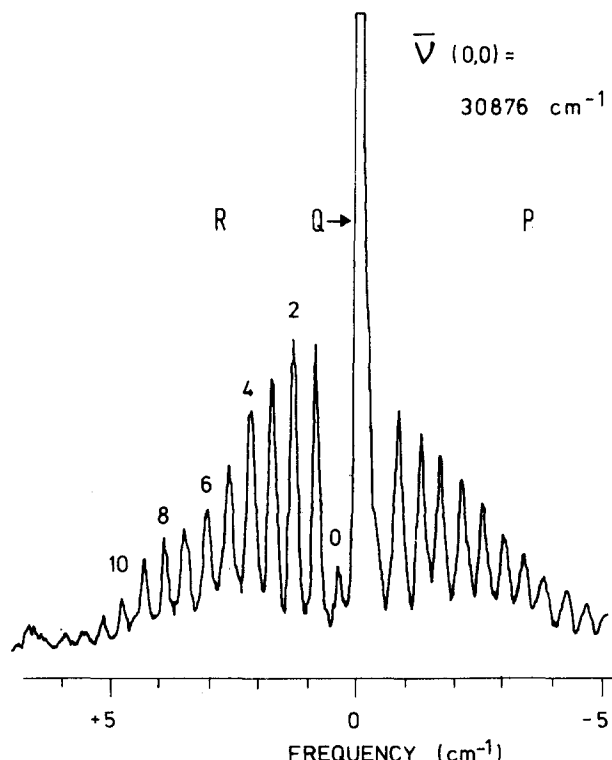

FIG. 1. Fluorescence excitation spectrum of the (0,0) C-type band of the $^1B_{3u} \leftarrow {}^1A_g$ transition of pyrazine-h_4. Pyrazine seeded in helium, stagnation pressure 0.5 atm, excited 4.5 cm from the 0.1 cm diameter pulsed nozzle. The ground state values J'' of lines containing all the $\Delta K = 0$ transitions with $K \leq J''$ are indicated in the R branch.
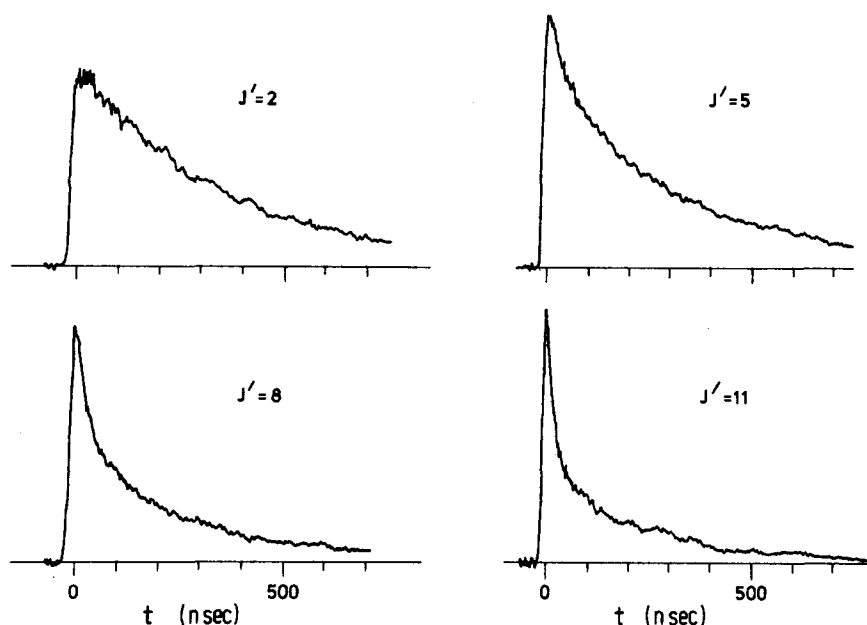
FIG. 2. Typical decays of pyrazine-h_4, showing rotationally dependent nonexponential behavior. Each decay is a sum over the decays of the K states belonging to one $J' \leftarrow J''$ transition.

which assumes a rigid symmetrical top, a Boltzmann distribution in the jet, and a K^2 dependence of the non-radiative rate. g_{JK} is the nuclear spin statistical weight. By further assuming that both the calculated and experimental decays are biexponential [i.e., of the form $I(J) = A^+ \exp(-t/\tau_1) + A^- \exp(-t/\tau_2)$], we obtain best fit values for the parameters a and f by comparing the experimental values of $A^+/(A^+ + A^-)$ with those found from curves generated by Eq. (1). Figure 3 shows the results obtained for $T = 10°K$, $B = 0.205$ cm^{-1},[6] $a = 1.2$ $\times 10^6$ sec^{-1}, and $f = 1.9 \times 10^6$ sec^{-1} for pyrazine-h_4; and $a = 9.0 \times 10^6$ sec^{-1} and $f = 2.5 \times 10^6$ sec^{-1} for pyrazine-

2,3-d_2h_2. The f values are very close to the total radiative rate of 1.2×10^6 sec^{-1} for the $(0, 0)$ band.[7]

The decay of $^1B_{3u}$ pyrazine following single rotational level excitation is reminiscent of the intermediate case behavior exhibited by several molecules in the bulk gas phase following single vibronic level excitation.[7-9] However, the value of A^+/A^- determined in our experiments is much less than unity for low J'. Since this value should be equal to the number of coupled levels, it appears that the model does not apply. An expression similar to Eq. (1) has been derived by Novak and Rice[10]
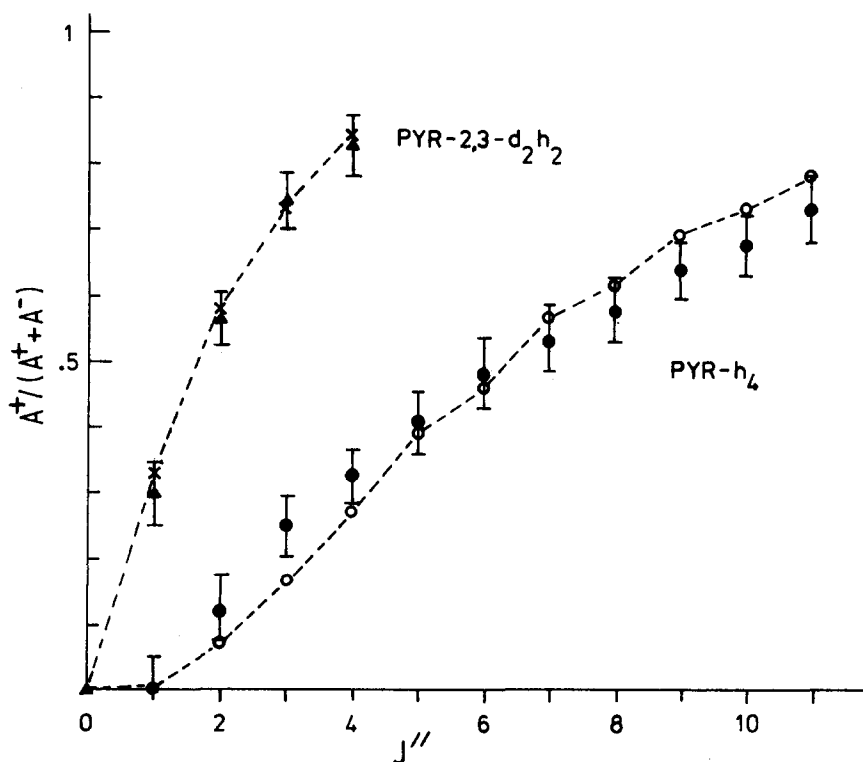

FIG. 3. Experimental (●, ▲) and calculated (o, X) values of $A^+/(A^+ + A^-)$ for pyrazine-h_4 and pyrazine-2,3-d_2h_2, respectively.

by considering the influence of Coriolis coupling on ra-
diationless decay but it is not clear why such coupling
should be important for the vibrationless singlet. How-
ever, the a values are of the order of magnitude ex-
pected for Coriolis effects involving the nuclei.[10] It is
possible that electronic Coriolis interactions[6] are pres-
ent. Also, if the process we are monitoring is inter-
system crossing, the effect could have its origin in a
K^2 dependence of the number of strongly coupled triplet
levels.[11] Whatever the mechanism, the results for py-
razine suggest that a rotational state dependence of the
radiationless rate might be expected in other large
molecule excited states as well, particularly those with
long radiative lifetimes.

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NOTES

14N nuclear quadrupole interaction in salicylaldoxime and in Cu(II) doped bis(salicylaldoxime) Ni(II)

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The study of changes produced by metal coordination
on the electronic distribution of N-containing ligands has
attracted considerable attention.[1,2] Sensitive techniques
such as level crossing double resonance (LCNDR) have
been used in obtaining information about the ^{14}N nuclear
quadrupole interaction (NQI) in powdered diamagnetic
samples.[2] The NQI is very sensitive to changes in the
N orbital population; therefore, new information may be
obtained about the changes in the N electronic distribu-
tion upon metal complexation by comparing the NQI in
both the free and complexed ligand. The interpretation
of the NQR data obtained in oxime powdered samples is
not unique as no information about the principal axes of
the electric field gradient (efg) tensor may be obtained
in such cases.[3] This problem seems particularly im-
portant in the interpretation of the ^{14}N NQR data in
oximes where the different orientation of the efg axes
cannot be obtained from other sources or chemical in-
tuition.[3] Unfortunately, there is no single crystal work
in oximes or their diamagnetic metal complexes that
could help in the interpretation of the quadrupolar data.
In magnetically diluted samples, the electron nuclear

double resonance (ENDOR) technique provides a way of
determining the components and the orientations of the
efg axes,[4] thus allowing a detailed analysis. In the
present paper, ^{14}N NQR data obtained in pure salicylal-
doxime (Sal) at 77 K and the quadrupole data obtained by
the ENDOR method in a single crystal of Cu(II) doped
bis(salicylaldoxime)[5] are compared. In Sal the popula-
tion of the N orbitals are similar to those found in sim-
ilar substituted aldoximes. From comparison of the
^{14}N NQR data in both the free and complexed Sal it was
found that a substantial amount of charge was trans-
ferred from the N nonbonding orbital upon metal com-
plexation (~ 0.35).

The values of the ^{14}NQR coupling constant (e^2Qq/h)
and asymmetry parameter η for Sal and related ald-
oximes, together with data for CuNisal and other related
metal oxime complexes, are shown in Table I. The ^{14}N
NQR spectrum of pure Sal was obtained at 77 K from a
commercially available sample without further purifica-
tion. The spectrometer employed consisted of a Robin-
son type oscillator modulated in frequency with a bidi-