Electronic relaxation of 1B3u(nπ*) pyrazine in a supersonic jet

ter Horst, Gerard; Pratt, David W.; Kommandeur, Jan

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.441468

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1981

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
LETTERS TO THE EDITOR

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area. (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 January 1981 for a fuller description of Letters to the Editor.

COMMUNICATIONS

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

Gerard ter Horst, David W. Pratt,* and Jan Kommandeur

Laboratory for Physical Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

(Received 22 December 1980; accepted 5 January 1981)

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 $K_0$ 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 jet4 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 $^1B_{3u} - ^1A_g(0, 0)$ 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 $v_{3a}$ 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 $10^4$ Å$^2$.

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 $\phi_j$ 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

$$I(J) = I_0 \sum_{J''} g_{J''} \frac{(J + 1)^2 - K^2}{J + 1} \exp\left[\frac{-BJ(J + 1) + \frac{1}{2}BK^2}{kT}\right] \exp[-(aK^2 + f)t],$$  

where $I(J)$ is the fluorescence intensity at rotational quantum number $J$, $I_0$ is the initial intensity, $g_{J''}$ is the degeneracy of the rotational level $J''$, $B$ is the rotational constant, $k$ is the Boltzmann constant, $T$ is the temperature, $a$ is the collision rate coefficient, and $f$ is a nonradiative rate coefficient. The fit of this expression to the experimental data is shown in Fig. 2.

FIG. 1. Fluorescence excitation spectrum of the $(0, 0)$ C-type band of the $^1B_{3u} - ^1A_g$ transition of pyrazine-$\beta_1$. 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.

which assumes a rigid symmetrical top, a Boltzmann distribution in the jet, and a $K^2$ dependence of the nonradiative rate. $K_{J'}$ 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 $T=10^7$K, $B=0.205$ cm$^{-1}$, $a=1.2 \times 10^6$ 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 $1.2 \times 10^6$ sec$^{-1}$ for the (0,0) band.$^7$

The decay of $1B_u$ 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.$^{10}$ 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. 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 $J' = J''$ transition.

FIG. 3. Experimental (o, •) and calculated (○, □) 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 radiationless decay but it is not clear why such coupling should be important for the vibrationless singlet. However, the $a$ values are of the order of magnitude expected for Coriolis effects involving the nuclei.\textsuperscript{16} It is possible that electronic Coriolis interactions\textsuperscript{4} are present. Also, if the process we are monitoring is intersystem crossing, the effect could have its origin in a $K^2$ dependence of the number of strongly coupled triplet levels.\textsuperscript{11} Whatever the mechanism, the results for pyrazine 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.

This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Dutch Organization for the Advancement of Pure Scientific Research (ZWO). D. W. P. thanks the Research Grants program of the North Atlantic Treaty Organization for the award of a travel grant.

\textsuperscript{a}Permanent address: Department of Chemistry, University of Pittsburgh, Pittsburgh, Penn. 15260.


\textsuperscript{3}C. Jouvet and B. Soep, J. Chem. Phys. 73, 4127 (1980).

\textsuperscript{4}G. ter Horst and J. Kommandeur (to be published).


\textsuperscript{8}R. van der Werf, E. Schutten, and J. Kommandeur, Chem. Phys. 11, 281 (1975); 16, 125 (1976); 16, 151 (1976).


\textsuperscript{11}C. Michel and C. Tric, Chem. Phys. 50, 341 (1980).

\section*{NOTES}

\textbf{14}N nuclear quadrupole interaction in salicylaldoxime and in Cu(II) doped bis(salicylaldoxime) Ni(II)

Juan Murgich

Centro de Quimica, Instituto Venezolano de Investigaciones Cientificas (IVIC), Apartado 1827, Caracas 1010-A. Venezuela

(Received 18 July 1980; accepted 12 November 1980)

The study of changes produced by metal coordination on the electronic distribution of N-containing ligands has attracted considerable attention.\textsuperscript{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 powderdiamagnetic samples.\textsuperscript{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 distribution upon metal complexation by comparing the NQI in both the free and complexed ligand. The interpretation of the NQR data obtained in oxide powder samples is not unique as no information about the principal axes of the electric field gradient (efg) tensor may be obtained in such cases.\textsuperscript{3} This problem seems particularly important 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 intuition.\textsuperscript{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,\textsuperscript{4} thus allowing a detailed analysis. In the present paper, $^{14}$N NQR data obtained in pure salicylaldoxime (Sal) at 77 K and the quadrupole data obtained by the ENDOR method in a single crystal of Cu(II) doped bis(salicylaldoxime)\textsuperscript{3} are compared. In Sal the population of the $N$ orbitals are similar to those found in similar substituted aldiximes. 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 transferred from the $N$ nonbonding orbital upon metal complexation ($\sim 0.35$).

The values of the $^{14}$NQR coupling constant ($e^2\eta q/h$) and asymmetry parameter $\eta$ for Sal and related aldiximes, 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 purification. The spectrometer employed consisted of a Robinson type oscillator modulated in frequency with a bidi-

\textbf{Letters to the Editor}