on the overall charge and the nature of the donor atoms but not on a precise geometrical arrangement of donor atoms, in contrast to the stable complex.

An interesting comparison may be made between the kinetic behavior of the monensin and cryptand (2,2,1) complexes. This is illustrated in Figure 4. The k_f values of (2,2,1) complexes[21] are, within experimental error, slower by a constant factor of 28, independent of the cation involved. Both systems also show an approximately linear relationship between log k_f and $(r_m)^{-1}$, where r_m is the ionic radius[28] of the cation involved. This constant difference between the formation rate constants for the two ligands can most readily be explained in terms of a difference in conformational energy required to allow replacement of cation–solvent with cation–ligand donor atom interactions during complexation. The cryptand (2,2,1) has a more rigid structure and so greater resistance to conformational change. The difference in energy required does not appear to depend upon the incoming cation. It should also be noted that the formation rates make no contribution to the relative selectivities of the two ligands.

The dissociation rates, on the other hand, show a rather sharper minimum for the Na^+ complex of (2,2,1) compared with that of monensin. Thus k_d values for $Na(2,2,1)^+$ vary over some 6 orders of magnitude and increase more sharply with both increasing and decreasing cation size on either side of Na^+. This is again in keeping with the relative flexibilities of the two ligands, as monensin should be able to adjust more easily to accommodate cations of non-optimum size and so show a somewhat smaller dependence upon the nature of the cation. The spherical cavity of the bicyclic cryptand, which leads to higher overall stabilities and lower cation dissociation rates, cannot adjust so easily to cations of different sizes, and this produces a larger variation in the dissociation rates among the cations.

Finally, a comment may be made concerning the formation rate constants for the Ag^+ complexes. These are at least 10 times higher than k_f values of alkali metal complexes of monensin and the cryptands (2,2,2) and (2,2,1) and approach the limit expected for a diffusion-controlled reaction. Similar results have also been found for AgMon complexes in other solvents[14] and $Ag(2,2,2)^+$ in water;[29] only in acetonitrile which is known to solvate Ag^+ very strongly do formation rates of Ag^+ and K^+ complexes become comparable.[29] This seems rather surprising as the overall solvation energies of Ag^+ cations are significantly higher than those of all alkali metal cations except lithium.[30,31] The reason for this apparent contradiction may lie in the fact that Ag^+ tends to form predominantly linear complexes with two ligands (or solvent molecules), involving partial covalent interactions.[32,33] It is possible that other coordinating positions are labilized by these stronger interactions and therefore can become coordinated to donor atoms of the macrocyclic ligands in the initial stages of the complexation reaction more readily than for the alkali metal cations. The dissociation rate constant for $Ag(2,2,1)^+$ is 4×10^5 times smaller than that of AgMon; this may be attributed to the strong $Ag^+ \cdots N$ interactions in the cryptand complex.

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Registry No. Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2; Ag, 7440-22-4; monensin, 17090-79-8.

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Spectroscopy and Dynamics of 9-Hydroxyphenalenone and of Its 5-Methyl Derivative in Solid Neon: Effect of Methyl Group upon Vibrational Relaxation

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Abstract: Spectroscopy and vibrational relaxation of 9-hydroxyphenalenone (9-HPLN) and of its 5-methyl derivative are examined and compared. Extensive vibrationally unrelaxed fluorescence is found for the unsubstituted 9-HPLN, which gives some qualitative insight into the pathways of vibrational relaxation in the S_1 state. Introduction of the methyl substituent results in at least an order of magnitude increase in the vibrational relaxation rates.

Low-temperature rare-gas matrices represent very useful model systems for studies of molecular relaxation processes.[1,2] Vibrational relaxation of small molecules in these weakly interacting inert "solvents" is often relatively slow, and one frequently observes unrelaxed electronic fluorescence originating from excited vibrational levels.[1] In larger molecules, however, with high intramolecular densities of states, vibrational relaxation is fast even in these cryogenic systems, and usually only fully relaxed fluorescence is reported. Very recently we have demonstrated that by using tunable pulsed dye laser excitation, coupled with time-resolved fluorescence detection, vibrationally unrelaxed emission may often be observable even in large molecular species. Thus, for example, unrelaxed fluorescence was observed for a variety of halobenzene radical cations.[3] Similarly, extensive vibrationally unrelaxed emission was reported for the even larger naphthazarin molecule.[4] The importance of such observations is that, in addition to the spectroscopic information obtained, one can also gain insight into the molecular relaxation and energy redistribution mecha-

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nisms. In this paper we extend such studies to several other compounds structurally and spectroscopically closely related to napthazarin.

We have noted above that in diatomic molecules in rare-gas matrices vibrational relaxation is often very slow. Thus N_2 in solid neon has a lifetime of the order of seconds,[5] while the decay of $X^2\Sigma^+$ CN vibrational levels occurs on a milliseconds time scale and is probably controlled by infrared radiation.[6] This is due to the large disparity between the molecular vibrational frequencies (>2000 cm^{-1}) and the frequencies of the lattice phonons ($\sim$50 cm^{-1}). To dissipate one vibrational quantum requires the creation of a large number of phonons—which is very inefficient and therefore a slow process. Such results are in agreement with expectations based on the "energy gap law", which predicts an exponential decrease in relaxation rates with increasing values of the molecular frequency.[7,8]

In light of the above discussion it was therefore quite surprising when it was established[9] that, for instance, $v = 1$ of $X^3\Sigma^+$ NH in solid neon ($\Delta G_{1/2} \sim 3146$ cm^{-1}) relaxes in $\sim$0.5 μs, at least seven orders of magnitude faster than N_2. Even more surprisingly, the corresponding deuteride, ND, was found to relax some three orders of magnitude slower than NH, in spite of the greatly reduced vibrational frequency ($\Delta G_{1/2} = 2328$ cm^{-1}). These observations were shown to be due to vibration–rotation coupling.[10] While vibrational frequencies scale with the square root of the reduced mass, rotational constants are proportional to the reduced mass itself. As a result, if the rotational local mode is the primary acceptor of the vibrational energy, relaxation of the deuteride will be a higher order and less efficient process, in spite of the lower value of its vibrational frequency. Similar relaxation behavior was later found in a variety of other small molecules.[11-14]

Clearly, the mechanism described above is not applicable to large rigid molecules such as naphthazarin which do not rotate in solid matrices and whose rotational constants and spacings are, in any event, very small. An interesting question arises, however, about the possible influence of the introduction into the molecule of a group which can undergo a free internal rotation or, at least, is characterized by a very low rotational barrier. To explore this question, we examine and compare in this paper vibrational relaxation in 9-hydroxyphenalenone[15,16] (9-HPLN) and in its 5-methyl derivative[16] (5-M-9-HPLN). The spectra of the 9-HPLN parent[17,18] and of its 2-methyl derivative[19] have been previously examined and are relatively well understood. The spectra of the 5-M-9-HPLN have, on the other hand, not yet been reported and we will therefore describe our spectroscopic observations prior to addressing the question of its vibrational relaxation.

Experimental Section

As in our previous work,[3,4] the compounds (9-HPLN and 5-M-9-HPLN) studied were vaporized from a quartz furnace and deposited on a 4 K metal mirror with an excess of matrix gas (argon or neon). In some experiments the samples were deuterated by proton exchange with excess D_2O.

The samples were excited by using a nitrogen laser pumped tunable dye laser. Fluorescence of the samples was collected by a lens, focused upon the entrance slit of a SPEX 14018 double monochromator, detected by an RCA C31034 photomultiplier, amplified, and digitized in a Biomation 8100 waveform recorder.

The monochromator or the laser were scanned by means of a minicomputer, which also processed the digitized data to produce the resolved emission or laser excitation spectra.

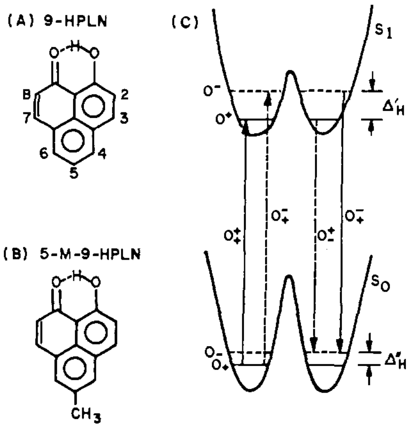

Figure 1. Structure of (a) 9-hydroxyphenalenone and (b) of its 5-methyl derivative. (c) Schematic showing splitting of the vibrationless levels as a result of the double-minimum potential and its consequences for spectral splitting of the O_0^0 transition. The solid arrows show spectrally allowed transitions; the formally forbidden O_-^+ and O_+^- transitions are denoted by dashed arrows.

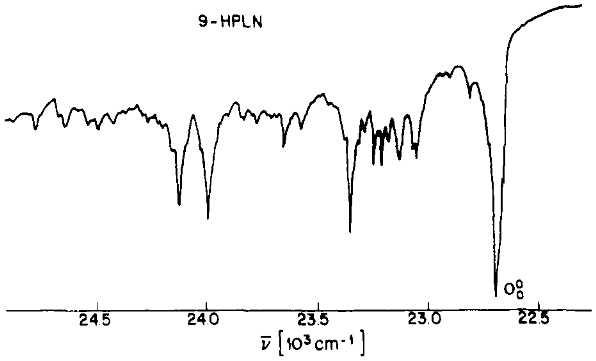

Figure 2. Absorption maximum of 5-methyl-9-hydroxyphenalenone (5-M-9-HPLN) in solid neon.

Results and Discussion

Spectroscopy and Structure of 9-hydroxyphenalenone. Spectra of unsubstituted 9-HPLN are now relatively well understood.[17,18] The molecule (see Figure 1A) contains a strong intramolecular hydrogen bond between the phenolic hydrogen and the carboxylic oxygen. This hydrogen bond is characterized by a symmetric double-minimum potential, since transferring the hydrogen completely from one oxygen to the other results in an equivalent, isoenergetic structure. The barrier separating the two equivalent minima is relatively low, and as a result, a splitting of the individual vibronic levels will take place. Recent matrix laser induced fluorescence studies were successful in measuring directly the respective tunneling splittings of the vibrationless level in 9-DPLN[17] and 9-HPLN[18] both in the ground state and in the first excited singlet state.

The effect of ring substitution upon the hydrogen-bonding potential is of considerable interest in its own right. In a rare-gas-matrix study, Rosetti et al.[19] have investigated the spectra of the 2-methyl derivative, 2-M-9-HPLN. In the presence of an asymmetrically placed methyl group, the molecular symmetry is lowered and the two minima of the hydrogen-bonding-potential function are no longer equivalent. They are found to be separated by $\sim$180 cm^{-1}, with the ground-state vibrational wave function being substantially localized in the deeper well.

The 5-M-9-HPLN isomer,[16] even though in many respects equally interesting, has, to our knowledge, not been previously spectroscopically studied. Substitution in the 5-position will,

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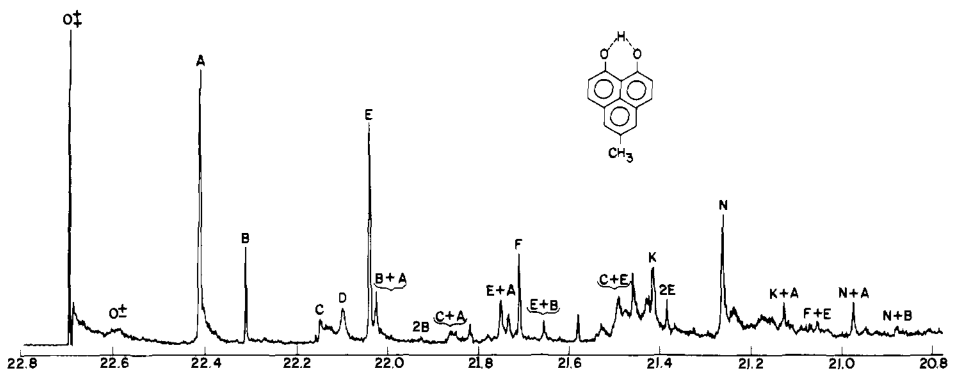

Figure 3. Fluorescence spectrum of 5-methyl-9-hydroxyphenalenone in solid neon.

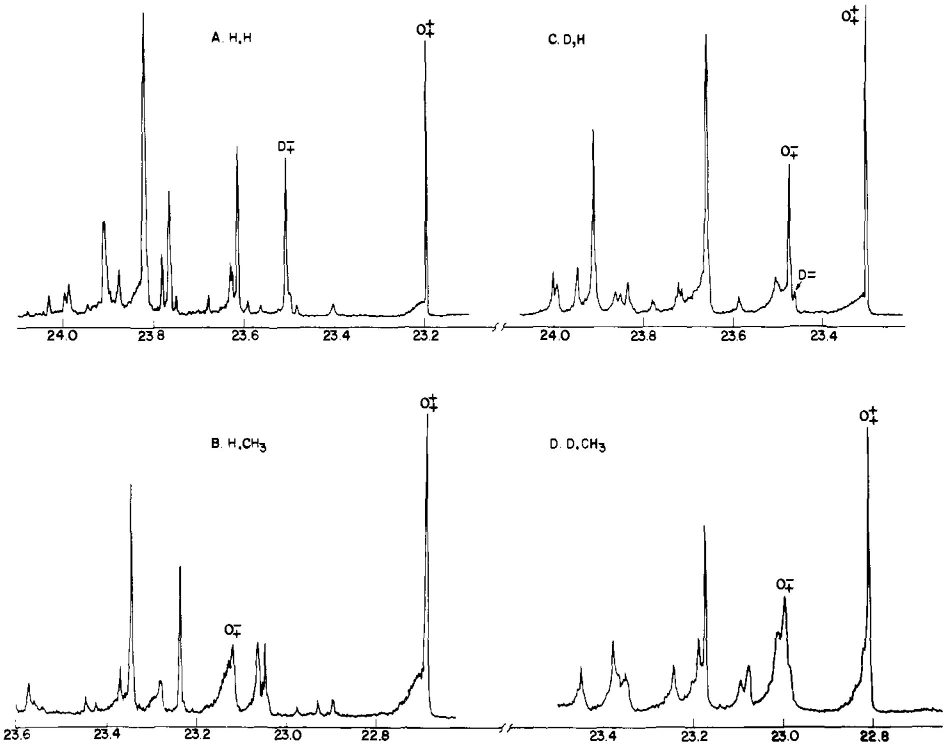

Figure 4. Laser excitation spectra of the vibrationally relaxed fluorescence of 9-hydroxyphenalenone and its derivatives in solid neon: (A) 9-HPLN, (B) 5-M-9-HPLN, (C) 9-DPLN, and (D) 5-M-9-DPLN.

assuming a freely rotating methyl group, not lower the molecular symmetry, and the two minima associated with the hydrogen bond will remain equivalent. The methyl substituent can, however, interact with the carbon–oxygen bonds through the π-electron network and affect in this way the height of the hydrogen bond barrier, which in turn should be reflected in the vibrational structure and spectroscopy of the compound.

Spectra of 5-M-9-HPLN. The absorption spectrum of 5-M-9-HPLN is shown in Figure 2. The spectrum has a strong origin band at 22 694 cm^{-1} and extensive vibronic structure at higher energies extending with gradually decreasing intensities beyond 26 000 cm^{-1}. When compared with the unsubstituted 9-HPLN, the origin is red shifted by over 500 cm^{-1}. This shift is, in spite of the greater distance of the substituent from the chromophore, much larger than the ~35-cm^{-1} red shift of the 2-methyl derivative. Replacing the phenolic hydrogen of 5-M-9-HPLN by deuterium results in a substantial blue shift of the origin band to 22 813 cm^{-1}.

Both 5-M-9-HPLN and 5-M-9-DPLN fluoresce strongly in solid neon. A fluorescence spectrum of the former compound, shown in Figure 3, exhibits a fairly close similarity to that of the unsubstituted HPLN, and to some extent also to the spectrum of naphthazarin. Three low-frequency vibrations at 284, 384, and 654 cm^{-1} are prominent in the spectrum; these are analogues of the 282, 429, and 629 cm^{-1} frequencies appearing in the spectrum of HPLN. In the deuterated compound the frequencies shift slightly to 290, 384, and 652 cm^{-1}, respectively. The stronger fluorescence bands of both compounds are compiled in Table I. The spectra are, compared with naphthazarin fluorescence, much less regular, with fewer identifiable overtone and combination bands.

The absorption and laser excitation spectra are even less regular than the emission spectrum and change profoundly upon deuteration. The presence of temperature-dependent "hot bands" in the matrix excitation spectrum as well as observations of vibrationally unrelaxed emission were instrumental in unraveling the spectra of HPLN and DPLN. No temperature-dependent features were present in the spectra of the 5-methyl-substituted derivatives and as we will discuss later, no vibrationally unrelaxed emission was observed. Fortunately, with the aid of the 9-HPLN spectra, it is still possible to assign fairly unambiguously the vibronic structures of the 5-methyl derivatives. In Figure 4, the low-energy regions of the spectra of 5-M-9-HPLN and 5-M-9-DPLN are compared with the corresponding regions of the respective unsubstituted parents.

The lowest energy "vibronic" band in the spectrum of 9-DPLN in Figure 4C appears at 172 cm^{-1} above the O_+^+ origin. This band was assigned to the formally forbidden O_+^- transition into the higher O^- component of the vibrationless level. In the spectrum of the corresponding methyl derivative, 5-M-9-DPLN (Figure 4D),

Table I. Emission Bands of 5-Methyl-9-hydroxyphenalenone and Its Deuterio Derivative in Solid Neon (cm^{-1})

5-M-9-HPLN				5-M-9-DPLN			
$\bar{\nu}$	$\Delta\bar{\nu}$	$\bar{\nu}$	$\Delta\bar{\nu}$	$\bar{\nu}$	$\Delta\bar{\nu}$	$\bar{\nu}$	$\Delta\bar{\nu}$
22 694	O_+^+	21 580	1114	22 813	O_+^+	21 837	976
22 602	92 (O_+^+)	21 490	1204	22 523	290 (A)	21 586	E + A
22 410	284 (A)	21 458	1236	22 429	384 (B)	21 561	1252
22 510	384 (B)	21 414	1280 (F)	22 261	552 (C)	21 546	1267
22 149	545 (C)	21 385	2 D	22 240	2 A	21 504	1309
22 099	595	21 262	1432 (G)	22 161	652 (D)	21 392	1421
22 040	654 (D)	21 128	A + F	22 139	A + B	21 242	1571
22 026	A + B	21 053	D + E	21 970	843	21 226	1587
21 750	A + D	20 975	A + G	21 945	868	21 095	1718
21 733	961	20 880	B + G	21 930	883		
21 709	985 (E)	20 761	D + F	21 873	940 (E)		
21 655	B + D	20 607	D + G	21 850	963		

Table II. Excitation–Absorption Bands of 5-Methyl-9-hydroxyphenalenone in Solid Neon (cm^{-1})

5-M-9-HPLN				5-M-9-DPLN	
$\bar{\nu}$	$\Delta\bar{\nu}$	$\bar{\nu}$	$\Delta\bar{\nu}$	$\bar{\nu}$	$\Delta\bar{\nu}$
22 694	O_+^+	23 773	1079	22 812	O_+^+
22 903	209	23 903	D + C	23 001	189 O_+^-
23 054	360 (A)	23 995	1301 (E)	23 239	268
23 069	375 (B)	24 127	1433 (F)	23 176	364 (A)
23 125	431 O_+^-	24 428	E + O^-	23 192	380 (B)
23 243	549 (C)	24 499	F + B	23 249	437
23 286	592	54 546	E + C	23 357	545
23 351	657 (D)	24 649	E + D	23 383	571
23 376	682	24 680	F + C	23 455	643 (D)
23 431	737	24 784	F + D	23 530	718
23 453	759	25 082	2388	23 763	951
23 578	884	25 296	2 E	23 818	1006
23 651	957	25 332	2638	23 972	1160
23 684	990	25 428	F + E	24 079	1267 (E)
23 708	D + A			24 248	1435 (F)

a strong band appears at O_+^+ + 189 cm^{-1}. The tunneling splitting increases substantially in 9-HPLN, when compared with 9-DPLN and the O_+^- transition shifts to O_+^+ + 311 cm^{-1}. Similarly, in the spectra of the 5-methyl derivatives, the O_+^+ + 189 cm^{-1} deuteride band is missing in the spectrum of 5-M-9-HPLN and a new strong band appears at O_+^+ + 431 cm^{-1}. In analogy with unsubstituted 9-HPLN, we assign these low-frequency bands, exhibiting large deuteration effect, to the O_+^- transition. It may be noted in Figure 4 that both the O_+^+ + 431 cm^{-1} band of 5-M-9-HPLN and the O_+^+ + 189 cm^{-1} band of the deuteride are rather broad, in fact considerably broader than other vibronic bands. Previously, we have shown that for several matrix-isolated benzenoid cations, such as $C_6F_6^+$ and $C_6H_3F_3^+$, the vibrational modes associated with the Jahn–Teller distorted potential are particularly sensitive to medium perturbation and often exhibit larger "inhomogeneous broadening" than modes not involved in the Jahn–Teller effect. The broad appearance of the "tunneling mode" of 5-M-9-HPLN is probably due to the same medium effect upon the double-minimum hydrogen-bonding potential. A summary of the stronger bands appearing in the absorption–excitation spectra is given in Table II.

Hydrogen Bonding in 5-M-9-HPLN. Analysis of the spectra presented above indicates that methyl substitution in the symmetric 5-position increases the tunnelling splitting of the vibrationless level of the upper state of 9-HPLN from 311 to 431 cm^{-1}. At the same time, the corresponding splitting increases from 172 to 189 cm^{-1} in the deuteride. Expanded traces of the 5-M-9-HPLN fluorescence spectrum exhibit a rather broad band 92 cm^{-1} below the O_+^+ origin. We assign this band to the O_-^+ transition, indicating that in the ground state also the tunneling splitting is increased from the 69 cm^{-1} 9-HPLN value. In the limit of weak hydrogen bonding, in order to transfer the hydrogen atom, one would have to rupture the OH band, and the height of the central potential barrier would approach the OH bond dissociation energy. On the other end of the scale in a "perfect" hydrogen bond, both oxygens would be equally strongly bound to the hydrogen atom, and there would be no central barrier in the bonding potential. Clearly, the relatively low hydrogen-bonding barrier of HPLN is further decreased by the 5-methyl substitution, and if one extends the above correlation between the barrier height and the strength of the hydrogen bond, one has to argue that the hydrogen bond is strenthened in the 5-M-9-HPLN.

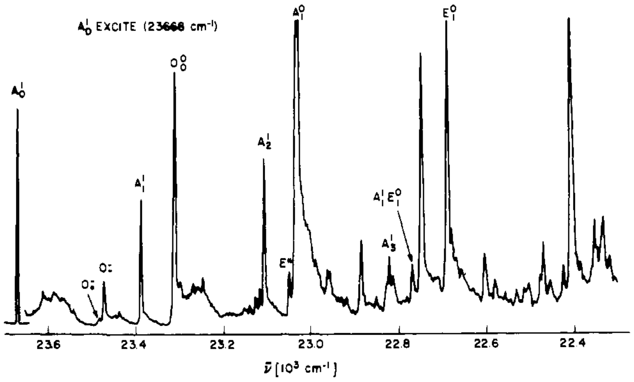

Figure 5. Fluorescence spectrum showing vibrationally unrelaxed emission of 9-DPLN; a level at O_+^+ + 359 cm^{-1} was excited.

It is interesting that exactly the opposite conclusion was inferred from the differences in the NMR chemical shifts of the hydroxylic protons between the two compounds.[16] However, a recent study of deuteron quadrupole coupling constants in these molecules found relative hydrogen bond strengths in agreement with the present investigation.[20]

Vibrational Relaxation of 9-HPLN and 9-DPLN. It is usually assumed that vibrational relaxation of large molecules in condensed systems is fast and that, regardless of excitation wavelength, electronic fluorescence will always originate from the vibrationless level of the excited state. As noted before, several recent experiments have demonstrated that, at least for molecules isolated in low-temperature matrices, this is not necessarily the case and that vibrationally unrelaxed fluorescence is often readily observed.[3,4] Very recently we have shown that this is the case also in matrix-isolated 9-HPLN.[18] This is exemplified in Figure 5 by a section of the fluorescence spectrum obtained by exciting the deuterated 9-DPLN with a laser tuned into resonance with the O_+^+ + 311 cm^{-1} vibronic level. Comparison with the spectrum resulting from excitation of the O_+^+ origin shows clearly that in addition to the relaxed fluorescence numerous extraneous bands are present in the spectrum, several of them at energies higher than the origin. These bands are readily assigned to both resonant emission from the O_+^+ + 311 cm^{-1} level as well as to partially relaxed fluorescence from a level at O_+^+ + 172 cm^{-1}, which was identified as the upper "tunnelin" component of the vibrationless level.[17,18]

In a similar way one may observe vibrationally unrelaxed fluorescence for various other excitation energies. Experimentally we find that for excitation of most vibronic bands with less than

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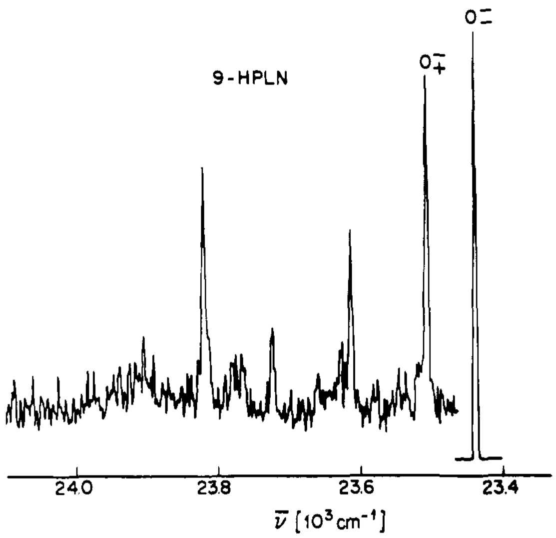

Figure 6. Example of an excitation spectrum of the vibrationally unrelaxed 9-HPLN fluorescence. The O_-^- transition at 23 450 cm^{-1} was monitored.

~2000 cm^{-1} of vibrational energy, the vibrationally unrelaxed emission is readily observable. Unfortunately, the lifetimes of the individual excited vibrational levels are too short for direct time-resolved measurement. The fluorescent emission, however, provides a convenient internal "clock" permitting the deduction of approximate lifetimes from spectroscopic observations. The radiative lifetimes and radiative rates of different vibrational levels of the same electronic state are usually very similar. If two or more vibrational levels are sequentially populated in a relaxation cascade, their relative overall emission intensities will be to a good approximation proportional to their lifetimes.

If the lifetime of one such sequentially populated level is known from direct measurement, one can, from the relative intensities of the unrelaxed fluorescence, estimate the absolute vibrational relaxation rates and lifetimes. In several recent studies we have thus, using the measured lifetime of the relaxed fluorescence, obtained the lifetimes of the excited vibrational levels. For example, in naphthazarin, the deduced lifetimes spanned the range of 10–300 ps, surprisingly long considering the size of the molecule.

Unfortunately, in the present case of 9-HPLN the lifetime of the relaxed fluorescence was not measured, and we can therefore not get a quantitative estimate of the relaxation rate. Qualitatively one may observe that for comparably concentrated samples the absorptions of naphthazarin and 9-HPLN matrices were comparably strong and that the radiative rates and lifetimes of the two related compounds may be quite similar. Since, furthermore, the unrelaxed 9-HPLN emission appears with intensities comparable to those observed in naphthazarin, we conjecture that also the relaxation rates of the two molecules in rare-gas matrices are similar and that the lifetimes of the longest lived, low vibrational levels of 9-HPLN (and 9-DPLN) are of the order of 100 ps.

In addition to providing information about the magnitude of the relaxation rates, the study of the unrelaxed emission, perhaps even more importantly, provides some insight into the mechanisms and pathways of the relaxation process. Such examination shows, like the more extensive investigations of naphthazarin, that the relaxation proceeds neither sequentially, through smallest increment steps, nor by a random energy redistribution, but via specific preferred pathways. This can be exemplified by the excitation spectrum of the unrelaxed fluorescence in Figure 6, which was obtained by monitoring the O_-^- emission band and scanning the laser. Comparison with the excitation spectrum of the relaxed fluorescence in Figure 2B shows that the lowest excitation maximum is the O_+^+ + 311 cm^{-1} band. This is quite understandable, since that band was assigned to the O_+^- transition and corresponds therefore to the minimum energy needed to populate directly the emitting level. All the higher energy levels appear in the spectrum with reduced relative intensities, reflecting the fact that the probability of their relaxation via the emitting O^- "tunneling" level is less than unity. While, however, for some levels (e.g., the O_+^+ + 416 cm^{-1} or O_+^+ + 622 cm^{-1} levels) the reduction is relatively minor, suggesting that they have sizable probability of relaxing via the O^- level, other levels (such as the O_+^+ + 566 or O_+^+ + 709 cm^{-1}) are almost completely absent, indicating that during their relaxation the O^- level is completely bypassed.

A similar pattern emerges from the analogous excitation spectra of fluorescence from other levels. For some of the levels the excitation spectrum consists of a single band: they are not substantially populated during the relaxation of other vibrational levels. They can only be efficiently accessed by direct optical excitation.

Effect of the Methyl Group: Relaxation of 5-M-9-HPLN. Figure 4, parts B and D, exemplifies the spectra obtained by excitation of higher vibronic bands of 5-M-9-HPLN and its deuterated derivative, respectively. Such spectra are individual with those obtained with O_+^+ origin band excitation. Except for occasional weak bands due to impurities or "site" effects, even expanded traces show no evidence of vibrationally unrelaxed emission. While again the lifetime of the compound has not been measured, it is unlikely to be strongly altered by the methyl substitution and the internal "clock" will run at the same rate as in unsubstituted 9-HPLN. One therefore has to conclude from the absence of unrelaxed emission that the vibrational relaxation in 5-M-9-HPLN is at least one order of magnitude faster than in the unsubstituted compound.

It is interesting to note that some time ago we reported extensive vibrationally unrelaxed emission in a variety of halogenated benzene cations.[3,21] On the other hand, a search for similar unrelaxed emission in, for instance, pentafluorotoluene cation and several similar methyl-substituted species proved unsuccessfull.[22] While the substitution of a hydrogen atom by methyl group increases the number of atoms in the molecule, we believe this in itself does not account for the increased relaxation rate. Thus in several dihydroxyanthraquinones (e.g. quinizarin), where one additional aromatic ring is added to the naphthazarin framework, extensive vibrationally unrelaxed fluorescence is readily observable.[22]

We propose that it is the insertion of the methyl group and introduction of low-frequency rotational—or librational—motion which is responsible for the increased efficiency of the relaxation process. Apparently the vibrational energy is more strongly and efficiently coupled to the low-frequency intramolecular motions than to the delocalized lattice phonons.

Summary

Introduction of a methyl substituent into the symmetric 5-position of 9-hydroxyphenalenone results in an increase in the proton tunneling splitting and hence decreases the potential barrier, suggesting a slightly stronger hydrogen bond.

Extensive vibrationally unrelaxed emission is observed for both 9-HPLN and its deuterio derivative. Study of this unrelaxed fluorescence suggests that, as in other similar large molecules recently examined, the relaxation is unexpectedly slow. The relaxation is found to proceed neither sequentially via the smallest energy steps nor by a random energy redistribution, but by selective, specific pathways.

No unrelaxed emission is detected in methyl-substituted 5-M-9-HPLN suggesting greatly increased vibrational relaxation rates. This increase in relaxation efficiency is attributed to the presence of low-frequency modes associated with the freely rotating methyl group.

Registry No. 9-HPLN, 7465-58-9; 5-M-9-HPLN, 78837-89-5.

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[22] Bondybey, V. E., unpublished results.