Solvent Effect on Excited State Conformational Changes in CF$_3$NO

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Abstract: Time-resolved excitation and emission spectra have been observed for the A″ ^{1}n-π^* state of CF$_3$NO in H$_2$, Ne, Ar, N$_2$, and CF$_4$ hosts at 4.2 K. Both monomers and higher polymers are fluorescent. The monomer vibronic line shapes are principally low-frequency ν_{12} torsion Franck-Condon envelopes appropriate for an eclipsed $\leftarrow \rightarrow$ staggered electronic transition. The gas-phase potentials are unchanged in condensed phase. Partial fluorescence depolarization indicates that CF$_3$NO monomers freely rotate about the A inertial axis in the CNO plane. The staggered excited-state conformer is unaffected by solvation. We find no evidence for the proposed eclipsed excited-state conformer.

I. Introduction

How are molecular geometries and dynamical processes affected by solvation? CF$_3$NO is interesting in this respect because the first n-π^* excited singlet state in the gas phase is stable in two different conformations. Gordon et al.[1] concluded that this nondegenerate ^{1}A″ state near 14 000 cm^{-1} has two stable local minima in its potential energy surface: (I) an eclipsed geometry with fairly large angle θ between the CF$_3$ axis and the CN bond, and (II) a staggered geometry with smaller angle θ. The ground electronic state is only stable in an eclipsed form. The electronic absorption near 7000 Å consists of two allowed systems (I and II) which correspond to the two excited-state conformers. In this experiment we attempt to study the influence of solvation upon the relative stability of these two conformers, and to study radiationless transitions between the two conformers, by comparing the absorption and fluorescence of CF$_3$NO in solid hosts at 4.2 K.

II. Experimental Section

A pulsed, tunable dye laser ($\Delta\lambda \approx 0.2$ Å, $\Delta t \approx 8$ ns) irradiates CF$_3$NO-doped matrices, and the resulting time, wavelength, and polarization resolved fluorescence is observed. The apparatus has been previously described in detail.[2] A transient digitizer records the fluorescence time dependence at one emission wavelength and transfers this data to a small computer. Digital excitation spectra, normalized to the dye laser energy on a pulse by pulse basis, are obtained by computer integration of fluorescence occurring within a specified time window following the laser pulse. Part of the laser beam is split off and monitored by a Molectron J305 joulemeter. The joulemeter output is amplified and separately digitized by the computer.

III. Observations and Assignments

Excitation (6900 Å) of a 1:2000 CF$_3$NO:neon matrix (deposited near 4.2 K) produces the CF$_3$NO emission spectrum appearing on the right-hand side of Figure 1. This fluorescence appears without measurable (20 < ns) rise time and shows single exponential decay ($\tau = 285 \pm 5$ ns) over almost three decades of intensity. The spectrum is independent of excitation wavelength in the region 5800–7165 Å, and we conclude that the emitting species is vibrationally relaxed. The normalized excitation spectrum appears on the left-hand side of Figure 1. The lifetime is independent of emission wavelength in the range 7200–8700 Å.

The observed lifetime is much shorter than the purely radiative lifetime expected on the basis of the low f number (2 $\times 10^{-4}$),[3] and the lifetime must actually be controlled by radiationless transition. Recently time-resolved gas-phase fluorescence of CF$_3$NO has been observed (without spectral resolution) and the same conclusion was reached.[4] In the gas phase, copious photodecomposition accompanies visible excitation, as the CF$_3$NO bond energy is only 31 kcal/mol.[5]

However, in solid neon, prolonged irradiation of the matrix produces no permanent dissociation ("bleaching"); therefore we apparently have a transient cage effect with ultimate recombination of the two fragments.[6]

The spectra are moderately broad, and we have attempted to generate sharper spectra in other hosts. Solid H$_2$ conceivably could be a more weakly interacting host as it has a lower binding energy than solid Ne. In our open cycle liquid He cryostat, we are marginally able to prepare a solid H$_2$ matrix near 3.6 K. Figure 2 shows the emission spectrum observed from a 1:1000 CF$_3$NO:H$_2$ matrix. Similar CF$_3$NO emission bands, as in Figure 1, are observed with little improvement in fwhm; in addition, there is a second, broader underlying component. This broader underlying component has also been occasionally observed in neon matrices, where its relative intensity appears to be correlated with deposition at higher (6–8 K) temperatures where surface diffusion is faster. Figure 3 shows that in a N$_2$ matrix deposited at 6–8 K, this broad underlying component is essentially absent. However, if this matrix is subsequently annealed at 22 K for several minutes and then observed again at 4.2 K, some underlying broad component has grown in. Annealing at 30 K completely and irreversibly transforms the initially moderately sharp emission into broad emission. This behavior is expected if the broader components in all three matrices represent fluorescence from dimers and high polymers. In Figure 3, the monomer emission on the left-hand side shows a lifetime $\tau = 344$ ns. In the center panel the broad component shows $\tau = 257$ ns, while in the right-hand panel $\tau = 78$ ns. Apparently in N$_2$ host the 22 K annealing produces principally dimers of 257-ns lifetime, while the higher temperature annealing produces higher polymers of shorter lifetime.

The Figure 1 excitation spectrum is similar to the system II gas-phase absorption spectrum reported by Gordon et al., and can be easily assigned using the totally symmetric ν_4, ν_7, and ν_1 excited state frequencies reported by these authors. The observed band maxima wavelengths and assignments appear in Table I. The fluorescence spectrum, which has not previously been observed, is also readily assigned in Table I. Gordon et al. concluded that the system II bands populate a staggered excited state, as shown in Figure 4. We will demonstrate that the torsional potentials in the gas phase exist unchanged for CF$_3$NO in solid neon.

What process broadens the individual vibronic transitions in CF$_3$NO monomer? Vibronic line shapes of guest molecules in solid hosts normally consist of zero phonon lines (ZPL) and broad phonon wings.[7] This resolution of the line shape into two distinct parts theoretically occurs if the molecular internal vibrations lie much higher in frequency than typical lattice phonon frequencies ($\sim$40–80 cm^{-1}). The ν_{12} CF$_3$ torsion in
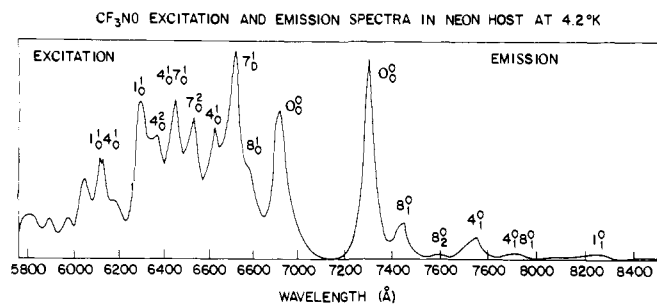
Figure 1. Digital emission and normalized excitation spectra of CF_3NO monomer in neon. Individual points are 3 Å apart; straight lines connect individual points. Assignments from Table I.
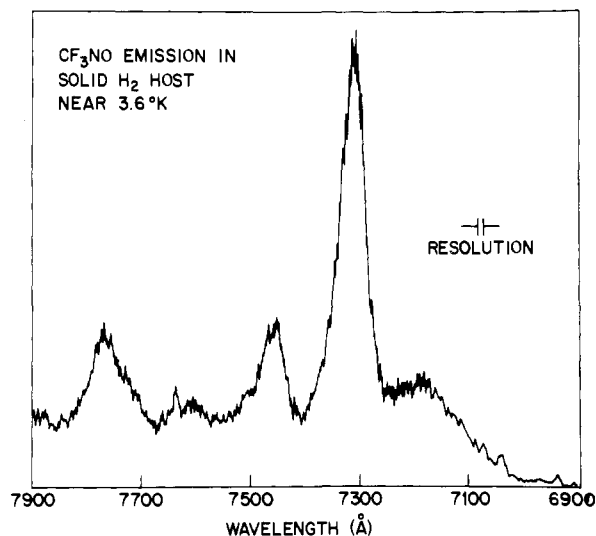

Figure 2. Emission spectrum of CF_3NO in a H_2 matrix, obtained with an electrometer–strip chart recorder combination. Excitation wavelength 6400 Å.
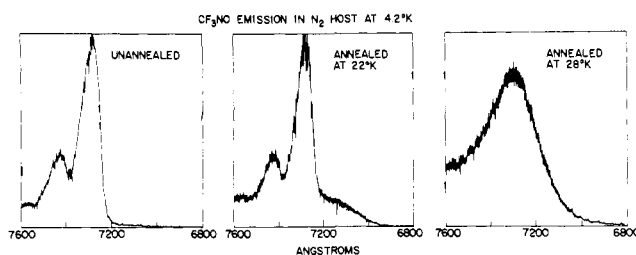

Figure 3. Emission spectra, as in Figure 2, for CF_3NO in N_2 host. Left panel: deposition at 6–8 K and spectra obtained at 4.2 K. Center panel: spectrum at 4.2 K of same matrix after annealing at 22 K for several minutes. Right panel: spectrum after annealing at 28 K for several minutes.

Table I. Assignment of Observed Structure for CF_3NO Excitation and Emission Spectra in Neon Host at 4.2 K[a]

	Excitation				Emission		
Intensity	Energy, cm^{-1}	ΔE, cm^{-1} (vac)	Assignment	Intensity	Energy, cm^{-1}	ΔE, cm^{-1} (vac)	Assignment
	13 953		12_0^0 [b]		13 592		12_0^0 [b]
	14 065		12_1^0 [b]		13 875		12_1^0 [b]
	14 168		12_2^0 [b]		13 805		12_2^0 [b]
7	14 472	0	0_0^0 [c]	10	13 698	0	0_0^0 [c]
5	14 771	295	8_0^1 (?) [c]	2.5	13 419	279	8_1^0 [c]
10	14 903	427	7_0^1 [c]	0.5	13 163	535	8_2^0 [c]
7	15 106	630	4_0^1 [c]	2.5	12 905	739	4_1^0 [c]
7	15 330	854	7_0^2 [c]	0.5	12 642	1002	$4_1^0 8_1^0$ [c]
8	15 523	1047	$4_0^1 7_0^1$ [c]		12 106	1592	1_1^0 [c]
6	15 716	1240	4_0^2 [c]				
8	15 898	1422	1_0^1 [c]				
3	16 171	1695	7_0^4 [c]				
5	16 342	1867	$1_0^1 7_0^1$ [c]				
4	16 545	2069	$1_0^1 4_0^1$ [c]				
2	16 747	2272	$1_0^1 7_0^2$ [c]				
2	16 984	2508					

[a] Torsion Franck–Condon maximum energies are accurate to ±5 Å. Zero phonon line (ZPL) energies accurate to ±0.5 Å. [b] ZPL. [c] Torsion FC maximum.

CF_3NO occurs near 78 cm^{-1} in the ground electronic state.[1] Torsional quanta and lattice phonons could in principle be strongly coupled; both types of low-frequency motions may contribute to the vibronic line shapes of the higher frequency modes active in Figure 1. Coupling to lattice phonons would be an external broadening process, while coupling to torsional quanta would be an internal broadening process.

There are two anomalies in the absorption and fluorescence spectra that normally do not occur in vibronic bands that are principally phonon wings. Table II shows that the fwhm values are almost insensitive to the physical properties of the host. In particular, the fwhm increases by a factor of 2 between Ne and CF_4, while the host polarizability increases by a factor of 10. This insensitivity suggests that the observed line shapes have a principally intramolecular origin.

A second anomaly is apparent in that the 0_0^0 band has a different line shape in absorption from that in fluorescence. To our knowledge such asymmetry never occurs for line shapes that are principally phonon wings.[8] Figure 5 shows the extreme red edge of the 0_0^0 excitation band, and extreme blue edge of the 0_0^0 absorption band in neon host. The true 0_0^0 ZPL (equivalently labeled 12_0^0) is observed as a weak, sharp feature at 7165 Å in both excitation and fluorescence spectra. The line shape asymmetry is shown by the fact that the 0_0^0 excitation maximum occurs 515 cm^{-1} blue of the ZPL while the 0_0^0 fluorescence maximum occurs only 269 cm^{-1} red of the ZPL. Moreover, Figure 5 contains additional structure that we interpret as ν_{12} torsion FC progressions in both absorption and fluorescence. There are additional excitation spectra ZPL (assigned as 12_0^1 and 12_0^2) at 7108 and 7056 Å, yielding ex-

cited-state torsional spacings of 112 and 103 cm^{-1}. In fluorescence there are two additional resolvable ZPLs, 12_1^0 and 12_2^0, yielding a ground-state torsional quantum of 78 cm^{-1}. These excited- and ground-state ΔG values are within 1 cm^{-1} of the corresponding gas-phase values. The agreement in the case of the excited state is striking as the gas-phase torsional barrier is only considered accurate to ≈20%.[1]

In the Figure 4 eclipsed ←→ staggered electronic transition, the strongest ν_{12} FC factors in absorption or vibrationally relaxed emission will connect $v = 0$ levels to high torsional levels at and above the free rotation barrier. The 12_0^0 band will be extremely weak, in agreement with our observations. If the observed absorption and emission vibronic line shapes principally represent torsional FC progressions, then the splitting between 12_0^0 and the band maximum approximates the torsional barrier height. These splittings in neon host yield excited-state and ground-state barriers of 515 and 259 cm^{-1}, which are in good agreement with the respective gas-phase values of 550 ± 20 and 269 ± 17 cm^{-1}.

Near the top of the barrier, the torsional levels will be more closely spaced. Our spectra do not show resolved ZPL for these strong transitions. Coupling with the neon lattice apparently broadens the individual ZPL, and creates lattice phonon wings connected to each ZPL, such that only the overall torsional FC envelopes are observed near the top of the torsional barriers.

In neon host, lattice phonon wings occur as continuous absorption between the barely resolved torsional ZPL in Figure
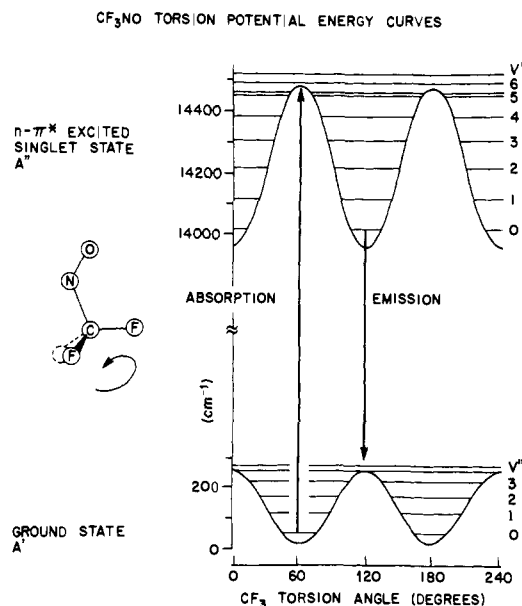
CF₃NO TORSION POTENTIAL ENERGY CURVES

Figure 4. Gas-phase system II torsional potential energy curves after Gordon et al. Vertical lines indicate expected strong Franck-Condon absorption and relaxed emission transitions. Ground state is eclipsed, and excited state is staggered.

5. In all other hosts the individual torsional ZPL are not observed.[9] In these more polarizable materials the coupling to the lattice is stronger, and the individual torsional ZPL are apparently less intense with respect to their phonon wings. In these hosts our only information about the torsional potentials is the splitting between the 0_0^0 band maxima in absorption and fluorescence. In neon host this splitting was interpreted as approximately the sum of the excited-state and ground-state torsional barriers. This splitting increases only slightly from 775 cm^{-1} in neon to 826 cm^{-1} in CF₄. This increase could represent a small change in the CF₄ barriers. It could also be that the barriers are unchanged, and the band maxima are shifted owing to an increased contribution by lattice phonon wings. In any event, a possible change in the torsional potential in the more polarizable hosts is small.

In an attempt to locate the eclipsed excited-state conformer, whose 0_0^0 band lies near 7300 Å in the gas phase, we have excited in the range 7165–7500 Å and have searched the $\lambda >$ 8000 Å region for emission. No new fluorescence could be detected. We also considered the possibility that the excited eclipsed conformer could radiationlessly feed the staggered conformer. However, no system I absorption bands appear in our excitation spectrum.

IV. Polarization

Photoselection experiments determine the direction of the fluorescence transition dipole with respect to the absorption dipole.[10] Neon matrices are glassy and transparent; therefore, experimental polarization ratios near the ideal photoselection limit can be obtained.[11] In neon we observe the *dimer* emission to exhibit P ($\equiv I_\parallel/I_\perp$) = 2.5 ± 0.1. P = 3.0 is expected for absorption and fluorescence by one nondegenerate transition dipole in a nonrotating species. We conclude that dimer emission corresponds to this case, with a slight experimental depolarization from 3.0 to 2.5. In this same neon matrix we observe P = 1.3 ± 0.1 for the *monomer* emission. The observed P is independent of excition and emission wavelength, and our observation of 12_0^0 in both excitation and emission spectra proves that the same excited state participates in absorption and in fluorescence. Almost certainly this excited state is singlet n-π* with a nondegenerate transition dipole ⊥ to the CNO plane. We must conclude that monomer CF₃NO rota-
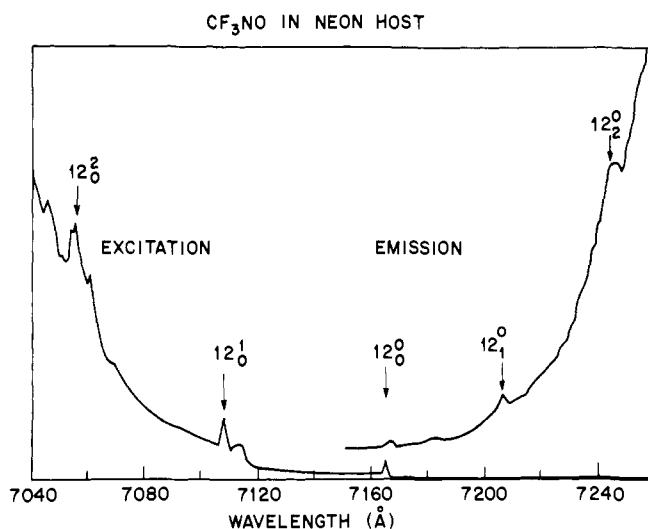
CF₃NO IN NEON HOST

Figure 5. High-resolution digital spectra of the Figure 1 0_0^0 fluorescence and absorption bands in the origin region. Small spikes are ν_{12} ZPL with assignments as given. The excitation spectrum also shows a second, minor CF₃NO site as a broader shoulder on the red side of each ZPL. Straight lines correct individual points, which are 1 Å apart.

Table II. 0_0^0 Torsion Franck-Condon Maxima and Widths in Both Emission and Excitation Spectra, as a Function of Host at 4.2 K[a]

ΔE	Host	Emission 0_0^0 peak	fwhm	Excitation 0_0^0 peak	fwhm	Lifetime $(10^{-9}$ s)
	H₂	13 680	112			51
775	Ne	13 697	94	14 472	125	285
783	Ar	13 605	148	14 388	135	
799	N₂	13 736	151	14 535	148	344
826	CF₄	13 740	226	14 556	254	244

[a] Entries in cm^{-1}. ΔE is Stokes shift between emission and excitation maxima.

tion partially depolarizes the resulting fluorescence. Actually P = 4/3 is expected if both absorption and emission dipoles lie in one plane. If CF₃NO is freely rotating about the lowest moment of inertia A axis (which lies in the CNO plane), then the transition dipole will be averaged over the plane ⊥ to this axis. Free rotation about A is consistent with P = 1.3 ± 0.1. Completely free rotation would yield P = 1.0. We conclude that CF₃NO monomers are rotating about the A axis on a time scale fast with respect to the excited-state lifetime τ = 285 ns.

V. CF₃NO Conformational Changes and Spectroscopy

The observed spectra are interpreted in terms of just one excited-state conformer. In neon host this ^{1}n-π* staggered conformer is red shifted by only $\simeq 30$ cm^{-1} with respect to the gas phase. The torsional potentials are unchanged from those in the gas phase (system II). There is no evidence for an appreciable host-induced increase in the torsional barrier of the type considered by Dellinger and Kasha.[12] These results support previous predictions of negligible change in solvated guest potential energy curves.[6] Owing to the extreme softness of weakly bound molecular hosts, guest motions and changes in geometry are easily accommodated. It is interesting that this statement is true even at the level of small ($\sim$100 cm^{-1}) guest quanta for the staggered conformer.

The absorption and emission vibronic FC patterns are not mirror images. In particular ν_7 is strong in absorption and yet weak in fluorescence. In the ground electronic state, both ν_4 and ν_7 are mixtures of skeletal bending and CN stretching motions.[13] In the excited ^{1}n-π* state, ν_4 and ν_7 probably are a somewhat different mixture of these motions. It might be,

then, that the geometry change between excited and ground states would occur as a motion along only ν_4 in the ground state, and along both ν_4 and ν_7 in the excited state. Such a change in the normal modes would explain why ν_7 is strong only in absorption.

The $^1n \rightarrow \pi^*$ electronic transition is formally allowed, yet quite weak ($f \simeq 2 \times 10^{-4}$). We observe that all of the totally symmetric FC progressions appear to be more intense in absorption. This could imply that these excited-state vibrations are active in borrowing oscillator strength from some higher electronic state of the same A'' symmetry.

There is no evidence in our data concerning the fate of the eclipsed excited state conformer. In the gas phase the eclipsed conformer actually lies several hundred cm^{-1} *below* the staggered conformer. This is a puzzling result. Gordon et al., studying condensed pure CF$_3$NO at 77 K, observed system II but not system I absorption. They suggested that the eclipsed isomer is somehow strongly blue shifted and broadened (perhaps entirely eliminated?) in condensed phase. This suggestion is difficult to understand theoretically. Recall that the eclipsed or staggered FCNO unit is rotating as a whole with respect to the neon host. Therefore, why should solvation have essentially no effect on both the eclipsed ground state and the staggered excited state, and yet strongly modify the eclipsed excited state?

Normally, drastic spectral changes accompany a drastic change in the *electronic* wave function, rather than a change in the size or conformation as determined by the geometry of the nuclei. For example, excited Rydberg[14] and charge-transfer[15] states have been observed to appreciably shift and broaden in rare gas hosts. One might conjecture that system I bands actually terminate on an electronically different excited singlet state. However, this possibility seems remote in view of extensive ab initio SCF CI calculations on CH$_3$NO that show only one excited singlet state below 7.14 eV.[16]

One might propose that in the gas phase the eclipsed conformer is nonfluorescent and in addition does not radiationlessly "feed" the fluorescent staggered conformer. In this case our data would not contradict the idea of negligible solvent effect, since we have no evidence that any change has occurred in going from gas phase to solid neon. However, negligible

solvent effect is not consistent with the conclusion of Gordon et al., that system I bands are strongly blue shifted in condensed CF$_3$NO. It is also difficult to understand why an unperturbed eclipsed conformer would be nonfluorescent, as the rate of radiationless transition into the eclipsed ground state should be similar to that of the observed fluorescent staggered conformer. Similar rates are expected if the geometry changes in the CNO chromophore upon electronic excitation are essentially the same.

We conclude that either the eclipsed conformer is strongly solvated for some unexplained reason, or the system I bands are hot bands of system II despite the conclusion of Gordon et al. Upon completion of this work, we learned of preliminary results by Spears and co-workers which suggest that system I bands actually are hot bands. If this is true then our expectation that either conformer would be negligibly solvated is correct.

References and Notes

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A Method of Describing the Charge Distribution in Simple Molecules

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Abstract: We present a simple method of representing the charge distribution in small molecules and apply the derived charge distributions to analyze the electrostatic potentials near these molecules as well as the structures and energies of intermolecular complexes. The molecules and ions discussed here are HF, H$_2$O, NH$_3$, HCl, H$_2$S, H$_3$P, F$_2$, H$_2$, N$_2$, Cl$_2$ SO$_2$, CO$_2$, HCN, HNC, H$_2$CO (ground and excited states), H$_2$NCHO, CH$_4$, CHF$_3$, NH$_4^+$, Li$^+$, F$^-$, CH$_3$NH$_2$, CH$_3$OH, CH$_3$F, C$_2$H$_4$, and C$_2$H$_2$.

Introduction

One of the goals of a chemist is to determine charge distributions in molecules. A knowledge of the charge distribution allows one to learn a great deal about its tendency to undergo covalent and noncovalent interactions with other molecules.

In this paper, we focus on noncovalent interactions and ask ourselves the question: what is the simplest method of representing the charge distribution which can qualitatively reproduce the magnitude and directionality of the electrostatic potential as well as the magnitude and directionality of inter-