Dual Fluorescence in Aromatic Nitriles: The Role of the Charge-Transfer State

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Dual fluorescence has been observed in the emission spectra of benzonitrile and tolunitrile seeded in a supersonic jet. This fluorescence has a sharp component that approximates the mirror image of the absorption spectrum and a broad, red-shifted component characteristic of emission from a charge-transfer state. In tolunitrile, the broad, red-shifted fluorescence is easily observed from all vibronic levels including the zero-point level. In benzonitrile, this component is weak in the lower vibronic levels. In both molecules, the intensity of the broad component increases with respect to the intensity of the sharp component as the energy of the initially excited level is increased. At the highest observed levels (approximately 1600 cm^{-1} above the zero-point level for both molecules), only the broad component is observed. The broad component is assigned to emission from a charge-transfer state. Ab initio calculations show that the charge-transfer state is much higher in energy than the S_1 state at the equilibrium geometry of the ground electronic state but is substantially lowered in energy as rehybridization of the cyano carbon from sp to sp^2 causes the −C−C−N to bend and the C−N bond to lengthen.

1. Introduction

The concept of a twisted-intramolecular-charge-transfer (TICT) state was proposed by Grabowski et al.[1] to explain the dual fluorescence in aminobenzonitriles in the condensed phase. In polar solvents, the dual fluorescence consists of a normal fluorescence which is the mirror image of the absorption spectrum and a red-shifted component from the TICT state. Aminobenzonitriles do not show red-shifted fluorescence in a supersonic jet; however, the anomalous emission for a van der Waals complex with a polar solvent molecule has been reported.[2] In this paper we report dual fluorescence in benzonitrile and tolunitrile in a supersonic free jet. The observation of this dual fluorescence suggested the interaction with a low-lying charge-transfer state and prompted calculations to elucidate the nature of this state. In these molecules the distortion of the red-emitting state cannot be a twist as in the TICT state. The theoretical calculations[3] suggest that the distortion that lowers the energy of the charge-transfer state in these molecules is a bending of the C−C−N bond angle away from the linear geometry of the ground electronic state.

Toluene and its derivatives have been of considerable interest to spectroscopists. Much of the work has focused on the torsional motion of the methyl group[4−6] and the effect of substituents on the torsional potential.[7] Fuji et al.[8] have extended their earlier studies and compared the influence of electron-donating and electron-withdrawing substituents on the barrier height for methyl rotation of the *o*-, *m*-, and *p*-toluene derivatives.

Toluene derivatives have also been of interest because of the role of internal, large-amplitude motion in vibrational relaxation. Smalley and co-workers studied vibrational relaxation in jet-cooled alkylbenzenes[9] and phenylalkynes.[10] Evidence for the participation of methyl rotation in vibrational level mixing is provided by comparing the single vibrational level fluorescence of *p*-fluorotoluene and *p*-difluorobenzene.[11−13]

Early fluorescence and absorption studies indicated that the lowest singlet excited state of benzene seems to be only slightly perturbed by the interaction of π-electrons of the cyano group.[14] On the other hand, Huang and Lombardi[15] observed a large nonlinear Stark effect on the 0−0 band of benzonitrile and attributed this to the coupling of the $^1B_2(\pi,\pi^*)$ state and a charge-transfer state. (Huang and Lombardi suggested that the charge-transfer state was a $^1B_1(n,\pi^*)$ state, but the relevant state calculated in ref 3 correlates to a $^1A_2$ state in C_{2v} symmetry.) The perturbation of the rotational structure of some bands[16,17] in benzonitrile has also been attributed to this coupling. There has been considerably less work on tolunitrile than on benzonitrile, but the charge-transfer interaction has also been proposed in tolunitrile.[18]

Lewis and Holman[19] were the first to use semiempirical theoretical calculations to suggest that the charge-transfer state of benzonitrile would be lowered in energy in a bent C−C−N geometry. More recently, Sobolewski and Domcke[3] used ab initio electronic structure calculations to demonstrate that the charge-transfer state in benzonitrile was lowered in energy by bending and stretching the cyano group. They suggested that, in addition to the TICT model, in aminobenzonitriles and some of their derivatives[20] a second charge-transfer mechanism would be the rehybridization of the cyano group (RICT model). These two channels may compete with each other in promotion of the charge-transfer emission in these compounds.

In this paper we observe the fluorescence excitation and dispersed emission spectra of benzonitrile and tolunitrile cooled in a supersonic free jet. Dual emission is observed from all vibrational levels of tolunitrile and from excited vibrational levels in benzonitrile. In both molecules the ratio of red-shifted to sharp fluorescence is increased with increasing vibrational excitation. Theoretical calculations on tolunitrile similar to those performed previously on benzonitrile indicate that bending the C−C−N angle also lowers the charge-transfer state in tolunitrile.

2. Methods

Samples of *p*-tolunitrile, benzonitrile, and toluene were purchased commercially (Aldrich) and used without further

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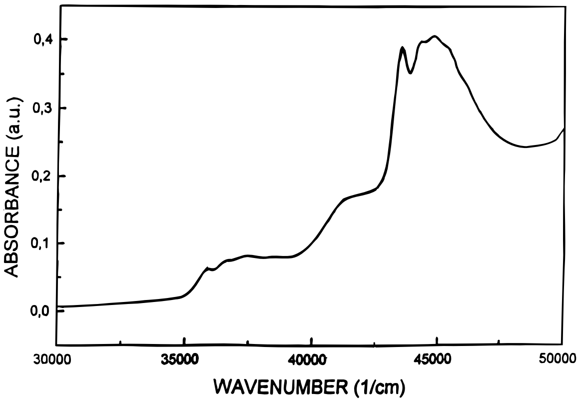

Figure 1. Absorption spectrum of *p*-tolunitrile in a static gas at 310 K.

purification. A continuous stream of helium at 3.5−5 atm pressure was passed over room-temperature samples of the organic molecules, and the mixture was expanded through a 100 μm pinhole.

The molecular jet was crossed by the output of a Nd:YAG pumped, frequency doubled dye laser. Fluorescence excitation spectra were taken by imaging the undispersed fluorescence from the jet on to a photomultiplier tube and measuring the fluorescence intensity as a function of the laser wavelength. Emission spectra were taken by tuning the laser to an absorption frequency, imaging the fluorescence on the entrance slit of a 1 m monochromator with 4 Å/mm dispersion, and recording the intensity as a function of the frequency of the emitted light. Emission spectra were taken with 1 mm slits, giving a resolution of 55 cm^{-1}. Details of the experimental apparatus have been described elsewhere.[21]

The theoretical ab initio calculations on benzonitrile were described in ref 3, and the calculations on tolunitrile reported here were done using the same methodology. The active space used in these calculations included the lone pair orbital of the nitrogen, the π_y* orbital of the CN group perpendicular to the π system of the ring, and all π orbitals parallel to the π system of the ring: eight for benzonitrile and nine for tolunitrile. Thus, the active space for benzonitrile consists of 10 electrons distributed over 10 orbitals, whereas for tolunitrile it consists of 12 electrons distributed over 11 orbitals.

3. Results

3.1. Experimental Results. Figure 1 shows the near-UV absorption spectra of tolunitrile vapor taken at 310 K. Maiti et al.[18] observed this spectrum and assigned the features at 36 204 and 43 185 cm^{-1} as the origins of the $^1L_b \leftarrow X$ and $^1L_a \leftarrow X$ transitions, respectively. The ^1L_b and ^1L_a states in *p*-tolunitrile are analogous to the $^1B_2$ and $^1A_1$ states, respectively, in benzonitrile, which has C_{2v} symmetry. Reference 18 does not show a figure of the tolunitrile spectrum and makes no mention of a feature near 41 000 cm^{-1}.

The supersonic jet fluorescence excitation spectra of toluene, benzonitrile, and tolunitrile in the region of the weak $^1L_b \leftarrow X$ transition are shown in Figure 2. The origins are at 37 477, 36 512, and 36 214 cm^{-1} for toluene, benzonitrile, and tolunitrile, respectively. Benzonitrile is known to form clusters in a supersonic jet, the weak bands to the red of the benzonitrile origin having been assigned to the dimer.[22] As seen in Figure 2, there are no dimer bands observable to the red of the tolunitrile monomer origin. At higher oven temperatures, a band appears at −98 cm^{-1} which might or might not be due to a dimer.

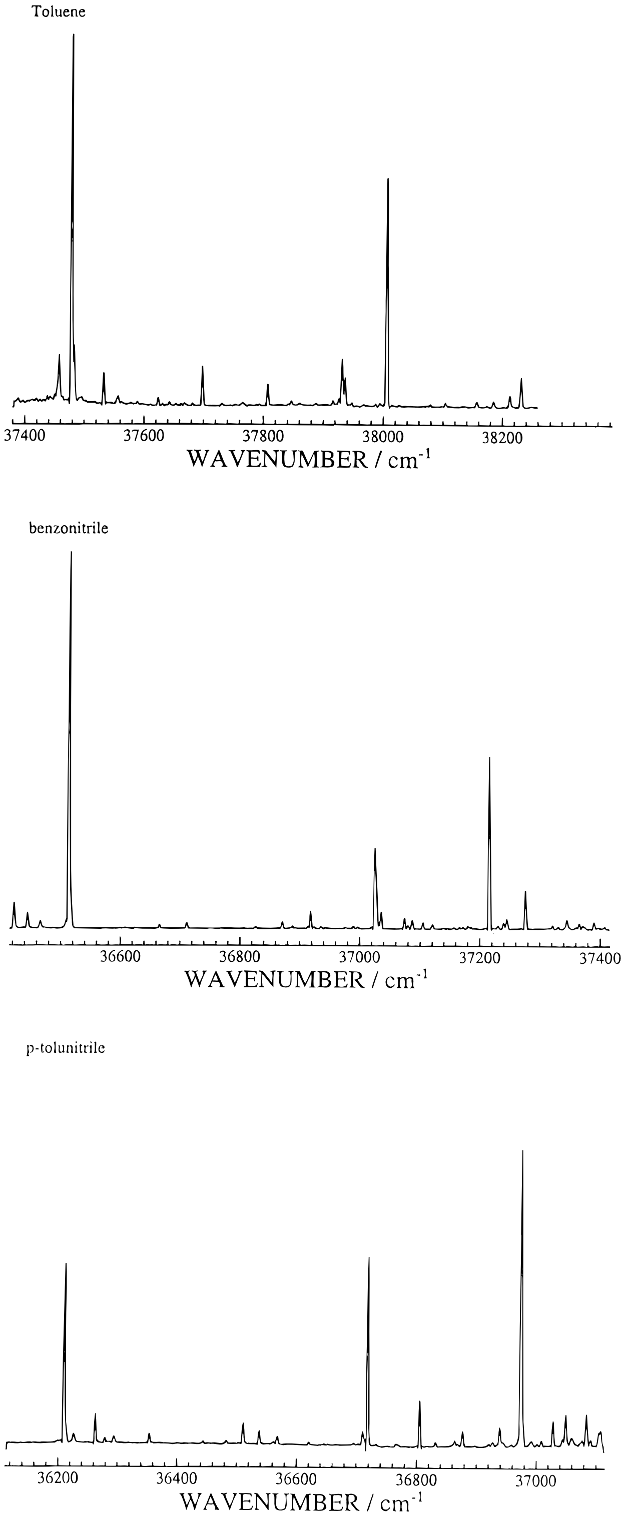

Figure 2. Portions of the laser-induced fluorescence excitation spectra around the origin of toluene, benzonitrile, and *p*-tolunitrile (P_0 = 3 atm of helium, nozzle and sample temperatures 300 K).

The fluorescence excitation spectra of the three molecules toluene, benzonitrile, and tolunitrile have many similarities. All three molecules have strong vibronic transitions at a frequency similar to the $6b^1_0$ (530 cm^{-1}) transitions in toluene, the analogous benzonitrile frequency being 517 cm^{-1} and the analogous tolunitrile frequency being 511 cm^{-1}. In toluene, odd-quantum transitions involving the nontotally symmetric vibration 6b are attributed to vibronic coupling with a higher electronic state.[9] We note that in tolunitrile the $6b^1_0$ transition is even more intense than the origin transition.

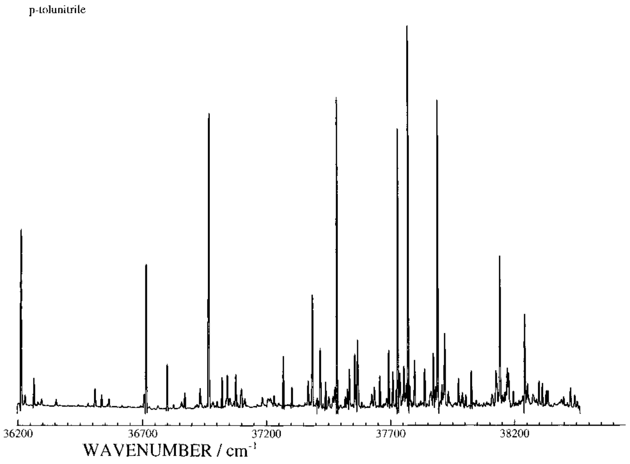

Figure 3. Laser-induced fluorescence excitation spectrum of *p*-tolunitrile in the region from 0 to 2000 cm^{-1} above the origin.

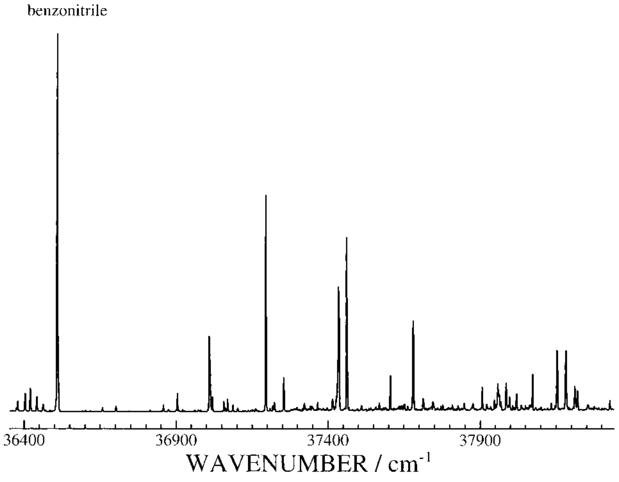

Figure 4. Laser-induced fluorescence excitation spectrum of benzonitrile in the region from 0 to 1800 cm^{-1} above the origin.

In addition to similarities in ring-mode frequencies, the vibrational frequencies associated with the motion of the methyl group are similar in toluene and tolunitrile and are also similar to those of *p*-fluorotoluene. Three observed methyl group frequencies are 14, 52, and 76 cm^{-1} in toluene,[23,24] 16, 52, and 84 cm^{-1} in tolunitrile, and 19, 53, and 78 cm^{-1} in *p*-fluorotoluene.[6] Combinations of these methyl group modes are seen with all the strong ring-mode vibrations. As seen in Figure 3, this leads to quite a complicated tolunitrile fluorescence excitation spectrum starting from around 1200 cm^{-1} excess energy. Nonetheless, in this region the spectrum can be resolved into many narrow individual features. The flourescence excitation spectrum of benzonitrile shown in Figure 4, while complicated, is less congested than that of tolunitrile.

The emission spectra that are produced when the origin transitions of benzonitrile and tolunitrile are excited are shown in Figure 5. The comparable emission spectrum of toluene can be found in ref 9. Like the fluorescence excitation spectra, the emission spectra are quite congested due to extensive vibrational activity. In addition to the many sharp spectral features, benzonitrile and tolunitrile also have a broad red-shifted background underlying the sharp features. In benzonitrile this background is weak and only observed with difficulty. However, the broad background in the tolunitrile spectrum is unmistakable, the ratio of the intensity of the sharp features to the broad background being 0.52 ± 0.03.

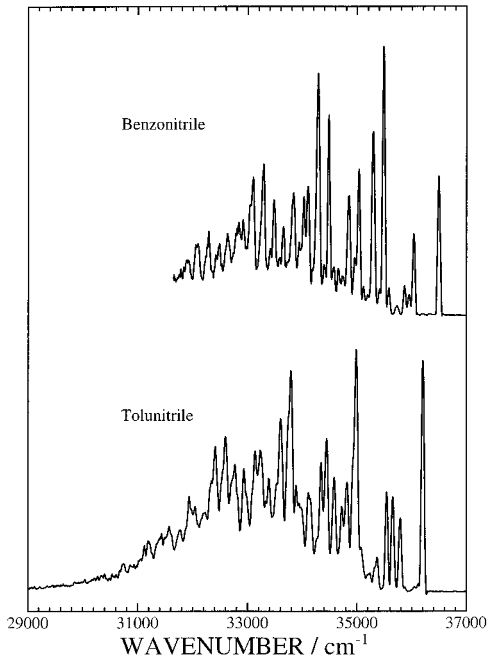

Figure 5. Dispersed fluorescence spectra of benzonitrile (top) and *p*-tolunitrile (bottom) obtained by excitation at the 0−0 band of the $^1B_2(\pi,\pi^*)$ electronic transition. The contribution of scattered light is insignificant in the benzonitrile spectrum but accounts for 30% of the intensity of the resonance transition in the *p*-tolunitrile spectrum.

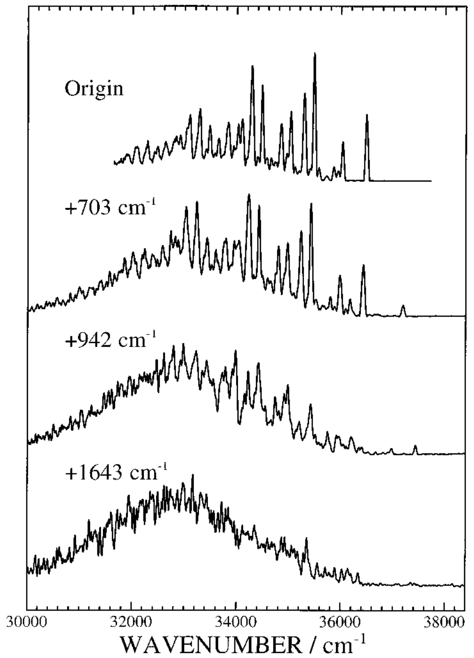

Figure 6. Dispersed fluorescence spectra of benzonitrile excited at the origin (36 512 cm^{-1}) and at successively higher vibrational levels. The contribution of scattered light is insignificant in these spectra.

In Figures 6 and 7 we show the emission spectra obtained by exciting various vibronic features in the fluorescence excitation spectra of benzonitrile and tolunitrile, respectively. In both cases, the broad, red-shifted part of the spectrum increases in intensity relative to the sharp features as the excitation energy is increased. At the highest excitation energies shown (1643 cm^{-1} for benzonitrile and 1174 cm^{-1} for tolunitrile), the sharp features are either very weak or, in the case of tolunitrile, missing entirely. The emission spectra of toluene shown in ref 9 show no distinct broad emission up to 965 cm^{-1} excitation energy, the highest level reported.

3.2. Results of Calculations. The ground-state geometry optimizations done at the HF/3-21G level were constrained to a given point group (C_{2v} for benzonitrile and C_s for tolunitrile).

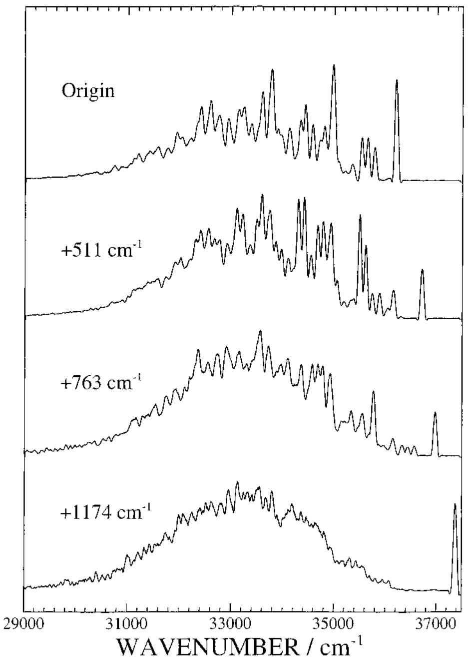

Figure 7. Dispersed fluorescence spectra of *p*-tolunitrile excited at the origin (36 214 cm^{-1}) and at successively higher vibrational levels. Scattered light accounts for 30%, 65%, 50%, and 100% of the intensity of the resonance features in the origin, $+511$ cm^{-1}, $+763$ cm^{-1}, and $+1174$ cm^{-1} spectra, respectively.

TABLE 1: HF/3-21G and CIS/3-21G Optimized Parameters of Geometry (Bond Lengths in angstroms, Bond Angles in degrees) and Energies (in au) of Tolunitrile in Its Ground and Charge-Transfer State

	ground state	CT state		ground state	CT state
1−2	1.390	1.403	6−1−2	119.6	118.9
2−3	1.378	1.372	2−1−7	120.2	121.9
3−4	1.390	1.396	1−7−8	180.0	126.5
4−5	1.386	1.390	3−4−11	120.1	119.6
5−6	1.382	1.378	3−2−9	120.4	121.1
6−1	1.387	1.395	2−3−10	119.5	120.2
1−7	1.428	1.441	5−6−13	120.3	121.2
7−8	1.141	1.301	6−5−12	119.4	120.1
4−11	1.516	1.513	4−11−14	111.1	111.3
2−9	1.071	1.071	4−11−15	110.5	110.3
3−10	1.072	1.072	5−4−11−14	0.0	0.0
5−12	1.072	1.071	3−4−11−15	59.8	59.6
6−13	1.071	1.071			
11−14	1.082	1.082	energy	−359.4597	−359.2536
11−15	1.085	1.085			
1−2−3	120.0	120.4			
2−3−4	120.9	120.4			
3−4−5	118.7	119.4			
4−5−6	120.9	120.3			
5−6−1	120.0	120.5			

The minimum calculated with a linear C−C−N group was found to be real by calculating the Hessian and observing that all vibrational frequencies were real. The geometric parameters for tolunitrile are listed in Table 1, and the geometric parameters for benzonitrile can be found in ref 3 (the numbering of the atoms is given in Figure 8). The lowest $^1(\pi,\pi^*)$ excited singlet states were optimized at the CIS/3-21G level and were also found to have a true minimum with a linear C−C−N group for both benzonitrile and tolunitrile. However, in both molecules, the next excited state (which is an n,π^* state in the linear C−C−N geometry) does not have a true minimum in the symmetric geometry but decreases by 2 eV in energy as the C−C−N is bent. Rehybridization of the cyano carbon from sp to sp^2 produces not only a bending of the C−C−N angle but also a lengthening of the C−N bond. The energy is at a minimum when the C−C−N bond angle is 126.5° (as compared to 180° in the ground state), and the C−N bond length is 1.30 Å (as compared to 1.14 Å in the ground state). This electronic state, a $^1A''$ state in C_s symmetry, changes orbital character as the C−C−N bond is bent, becoming dominated at the energy minimum by a single $\pi\sigma^*$ electronic configuration with the σ^* molecular orbital consisting mostly of the π_y in-plane orbital of the cyano group.

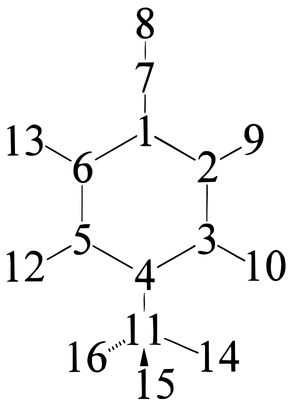

Figure 8. Structure of tolunitrile with enumeration of atoms indicated.

The bending of the cyano group in the excited state is in accord with Walsh's rules,[25] which were used to predict the bond angle of excited states of HAB-type molecules on the basis of the number of electrons. The lowest excited state of HCN is the $^1A''$ state which is produced by a $1a'' \rightarrow 7a'$ excitation.[26] The bond angle of this state is 125°, consistent with Walsh's predictions. In our molecules, the $^1A''$ state is dominated by the single $4a'' \rightarrow 24a'$ electronic excitation with the latter orbital almost entirely localized on the cyano group. This orbital is the analogue of the $7a'$ orbital in HCN, and it is therefore not surprising that the optimized value of the CCN angle in the $^1A''$ states of benzonitrile and tolunitrile is very close to the value observed in the lowest excited singlet state of HCN.

An analysis of the electron population on the atomic centers shows that the transition from the ground electronic state to the $^1A''$ state involves a significant amount of negative charge transfer from the ring to the cyano group. The resulting excess negative charge on the cyano group is responsible for the change of hybridization on the carbon atom from sp to sp^2. A normal-mode analysis performed at the C_s optimized geometry of the $^1A''$ state gives all real frequencies for both benzonitrile and tolunitrile.

As was the case in the benzonitrile calculation, the HF and CIS levels of theory that were used for geometry optimizations are too crude for reliable estimates of electronic state energies. This is particularly true for excited electronic states where the effect of dynamic electron correlation (neglected at the HF and CIS levels) becomes of crucial importance. Therefore, the energies of several low-lying singlet states of both molecules were recalculated with the use of the CASSCF/CASPT2 approach at the optimized ground state and $^1A''$ (CT) geometries. The results for benzonitrile were given in ref 3, and the results for tolunitrile are given in Table 2 and Figure 9, which also shows the benzonitrile results for comparison.

As was the case with benzonitrile, in general in the lowest electronic configurations the CASSCF reference function has a large weight. However, there are exceptions in the higher states where the reference weight is as small as 0.3. This result may be due to the interaction with intruder states which were not

TABLE 2: CASSCF and CASPT2 Energies (in au), Energies Relative to the Ground State [ΔE (eV)], the Weight of the CASSCF Reference Function in the First-Order Wave Function (ω), Dipole Moments [μ (D)], and Oscillator Strength (f) for Optical Transitions from/to the Ground State Calculated with DZP Basis Set for Tolunitrile at Molecular Geometries Optimized in the Ground and in the Charge-Transfer States

state	E_{CASSCF}[a]	ΔE_{CASSCF}	E_{CASPT2}[a]	ω	ΔE_{CASPT2}	μ	μ_{exp}[b]	f
			Ground-State Geometry					
S_0	−0.6794		−1.6809	0.749		4.65	4.40	
$^2A'$	−0.4975	4.95	−1.5121	0.730	4.59	4.45	5.23	0.0005
$^3A'$	−0.4057	7.44	−1.4627	0.722	5.93	8.30		0.240
$^1A''$	−0.3372	9.31	−1.4075	0.375	7.44	5.97		0.0
$^2A''$	−0.3650	8.55	−1.3875	0.242	7.98	1.12		0.0
			Charge-Transfer Geometry					
S_0	−0.6253	1.47	−1.6388	0.742	1.14	3.71		
$^1A''$	−0.4388	6.54	−1.4928	0.725	5.12	9.16		0.0015
$^2A'$	−0.4477	6.30	−1.4772	0.677	5.54	3.59		0.0015
$^2A''$	−0.3905	7.86	−1.4367	0.728	6.64	12.83		0.0
$^3A'$	−0.3785	8.18	−1.4211	0.301	7.07	2.46		0.0403

[a] Energy relative to −361.0 au. [b] Experimental value from ref 18.

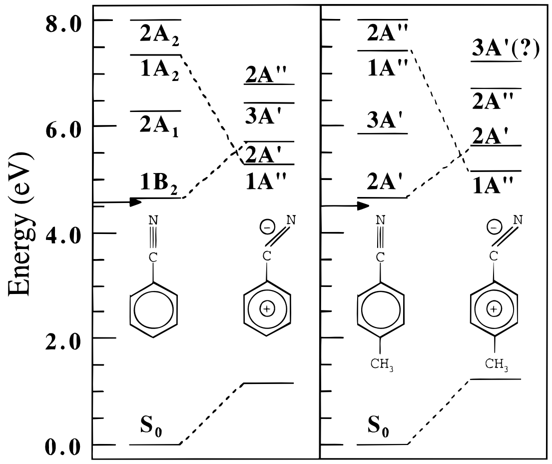

Figure 9. CASPT2/DZP energy level scheme of benzonitrile and tolunitrile calculated at the ground-state optimized geometry (dashed lines) and the charge-transfer optimized geometry (dotted lines). Solid lines denote energy calculated at the optimized geometry of this state. Arrows indicate the position of the experimentally observed 0−0 line in the $S_1 \leftarrow S_0$ absorption. Adiabatic corrections between the lowest excited states of the given symmetry (in the C_s point group) are indicated.

included in the active space and give an artificial energy shift (e.g., the 3A′ state at the CT geometry).

4. Discussion

The most striking feature of the benzonitrile and tolunitrile spectra is the broad, red-shifted feature in the emission spectrum that is produced even when the absorption feature that caused this emission is sharp. The intensity of the broad, red-shifted feature grows relative to the sharp, unshifted emission features as the excitation energy is increased, although in the case of tolunitrile it is clearly observable even at the 0−0 band. The growth of the broad, red-shifted feature and the decay of the sharp, unshifted features with increasing excitation energy indicates that the broad feature is not simply due to spectral congestion in a single electronic state.

This type of cold supersonic jet emission spectrum, a combination of broad, red-shifted emission and sharp, relatively unshifted components, has been seen in other molecules.[29,30] For *p*-fluorotoluene in a room-temperature static gas, Parmenter and Stone[11] observed the buildup of a broad, congested component for excitation of levels above 400 cm^{-1} excess energy. The resonance fluorescence was essentially gone when the excitation was above 1300 cm^{-1} above the origin. This effect was attributed to effective vibrational−rotational level mixing and enhancement of intramolecular vibrational redistribution. However, in the case of tolunitrile, the broad, red-shifted background underlying the sharp features can be observed in the emission spectrum produced by exciting the origin. Similar behavior is observed in benzonitrile following excitation in the 500−700 cm^{-1} region. In benzonitrile there is no methyl group to enhance IVR and to increase the density of states.

Other examples of dual fluorescence in a supersonic free jet have been explained by a three-state model including the ground electronic state (state 1), an excited electronic state (state 2) with potential surface similar to that of the ground state, and a second excited electronic state (state 3) with an equilibrium geometry significantly different from the other two states. In such a model, electronic transitions between the ground state and state 2 are dominated by $\Delta v = 0$ Franck−Condon factors. The emission spectrum produced by state 2 will be sharp and relatively unshifted from the excitation frequency. State 3 will not be directly excited (direct excitation only occurring at much higher energy) but can be populated by relaxation following excitation of state 2 as long as at some geometry state 3 is lower in energy than state 2, that is, if there is a crossing of the potential surfaces of state 2 and state 3. If state 3 is populated by relaxation from state 2, its emission spectrum will be dominated by $\Delta v \neq 0$ Franck−Condon factors, and as a result, emission will be from the low-energy vibrational levels of state 3 to the high-energy vibrational levels of the ground state producing a broad, red-shifted emission. It should be noted that in this model the width of the broad, red-shifted feature is not a homogeneous width produced by lifetime broadening. The width is a heterogeneous width caused by the superposition of many individual transitions. Because of the shift between the potential surfaces of states 1 and 3, emission is to a region of the potential surface of state 1 with a high density of states producing many individual transitions.

Recently, Helm et al.[27] observed the high-resolution spectrum of the origin transition of benzonitrile. From the observed line width of individual rotational features, they were able to place a lower limit of 1 ns on the lifetime of any nonradiative process. Since the fluorescence lifetime of benzonitrile is 70 ± 2 ns,[28] this observation is not in disagreement with our observations.

Even if the surfaces of states 2 and 3 do not cross, dual emission is possible as long as there is significant mixing of states 2 and 3. The mixed wave function of the excited state will produce dual emission partly characteristic of state 2 and partly characteristic of state 3. Of course, such extensive mixing is only likely if the energy gap between the two states is not too large.

Two examples of dual emission are the bichromophoric molecule anthracene−$(CH_2)_n$−dimethylaniline[29] and van der Waals complexes of two aromatic molecules that can form exciplexes.[30] In both these cases, state 2 was a locally excited $\pi-\pi^*$ state of one of the chromophores and state 3 was a charge-transfer state. The shift in potential surface between states 2 and 3 was caused by the Coulomb attraction between the two halves of the molecule in the charge-transfer state.

The spectra reported here do not involve two chromophores but are produced by a single molecule. Nonetheless, in light of the theoretical calculations, it is reasonable to invoke the same model that was used to explain this phenomenon in the cases of bichromophoric molecules. Here state 2 would be the $^1B_2$ state of benzonitrile and the analogous $^1A'$ state of tolunitrile. These are both $\pi-\pi^*$ states and have potential surfaces similar to that of the respective ground states. State 3 would be the $^1A''$ charge-transfer states of benzonitrile and tolunitrile which are high in energy at the equilibrium geometry of the ground state but fall significantly in energy as the CCN bond is bent. Absorption transitions between state 1 and state 2 would be sharp as would emission from state 2 to state 1, the biggest Franck−Condon factors for these transitions being $\Delta v = 0$ or a small integer. However, if there is relaxation to or mixing with state 3, the charge-transfer state, it will be to vibrational levels where the expectation value of the C−C−N angle is far from 180°. It should be noted that since states 2 and 3 belong to different representations in the C_s point group (A′ and A″), a nonadiabatic interaction involving out-of-plane modes is necessary to couple the locally excited state (2) and the charge-transfer state (3). In this case emission from state 3 will be to highly excited, bent vibrational levels of the ground state producing the broad, red-shifted component in the emission that we observe. The lowering of the charge-transfer state as the C−C−N angle is bent to allow coupling with the $\pi-\pi^*$ is consistent with the results of electronic structure calculations.

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