Structural information on the S_0 and S_1 state of o-fluorophenol by hole burning and high resolution ultraviolet spectroscopy

Karen Remmers and W. Leo Meerts
*Department of Molecular and Laser Physics, University of Nijmegen, P.O. Box 9010,
6500 GL Nijmegen, The Netherlands*

Anne Zehnacker-Rentien, K. Le Barbu, and F. Lahmani
Laboratoire de Photophysique Moléculaire, Université de Paris-Sud, Bât. 213, 91405 Orsay, France

The electronic transitions of o-fluorophenol situated at $36\,799.382$ cm^{-1} and $36\,906.710$ cm^{-1}, denoted the A and B bands, respectively, have been investigated by high resolution fluorescence excitation spectroscopy. Hole burning studies together with the high resolution spectroscopy results show that both bands originate in the same ground state and can be fitted to the rotational constants of the cis isomer. The rotational constants for the excited states are found to be $A' = 3231.795$ MHz, $B' = 2207.92$ MHz and $C' = 1313.97$ MHz for the A band and $A' = 3226.945$ MHz, $B' = 2211.24$ MHz and $C' = 1321.03$ MHz for the B band. The planarity of the ground state is lost upon electronic excitation, which enhances the activity of an out-of-plane vibration. The A and B band transitions arise from excitations to respectively the zero and first overtone levels in the double-minimum potential of this out-of-plane vibration, which shows similarities to the so-called butterfly mode observed in other benzene derivatives. © *2000 American Institute of Physics.* [S0021-9606(00)00314-7]

I. INTRODUCTION

Phenol and naphthol derivatives, substituted in ortho-position by a proton accepting group, provide model systems for studying the influence of intramolecular hydrogen bonding on the spectroscopic properties of the system.[1–7] However, these systems have two different isomers, differing by the direction of the hydroxyl group, as shown in Fig. 1 for o-fluorophenol. In the *cis* isomer an intramolecular hydrogen bond is formed between the hydroxyl group and the proton accepting group, which will stabilize it over the *trans* isomer.[8] The influence of rotamerism on the spectroscopy and dynamics of the S_1 state has especially been studied in ortho-halophenols, such as chlorophenol[2] and fluorophenol,[1] whose $S_0 - S_1$ electronic transition displays two strong bands in the region of the origin, denoted A and B hereafter.

In the past decades there has been much discussion about the nature of the A and B band in o-fluorophenol. First measurements of the electronic spectrum in the gas-phase were done by Tripathi in 1971.[9] Tripathi assigned the A band to the origin of the $A' \leftarrow A'$ transition, corresponding to the $B_{2u} \leftarrow A_{1g}$ transition of benzene, and the B band to a vibronic band, corresponding to an excited state fundamental of 109 cm^{-1}, since a vibration of this magnitude was also seen in o-fluoroanisole.[10]

Since the dispersed fluorescence spectrum, obtained by exciting the B band, failed to show a strong band corresponding to a fundamental vibration of around 109 cm^{-1}, Oikawa *et al.*[1] assigned the two bands to the origins of the two different isomers. The greater stability of the *cis* isomer was used as an argument to assign the (stronger) A band to the *cis* and the B band to the *trans* isomer.
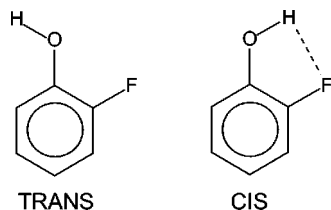
Measurements of the OH stretching vibration by Omi

et al.[11] contradicted these results. Using IR dip spectroscopy, they measured the OH stretching vibration via excitation of both the A and B states and in both cases found the same value (3634 cm^{-1}). This implies that both bands belong to the same isomer, since the intramolecular hydrogen bond in the *cis* isomer will cause a difference between the OH stretching frequency of the two isomers. A redshift to the phenol frequency (3658 cm^{-1}) of 24 cm^{-1} was observed. This is a typical shift for weakly hydrogen bonded OH and leads to the conclusion that both bands originate from the *cis* isomer. Fujii *et al.*[12,13] reached the same conclusion from the OH stretching vibration of the o-fluorophenol ion. Although no splitting in the OH stretching mode has been observed in the vapor phase, a splitting of the OH torsional frequency has been related to the presence of the two different isomers.[14]

The microwave spectra of o-fluorophenol and its deuterated derivative only show the presence of the *cis* isomer.[15] However, the authors did not rule out the existence of a *trans* isomer, since the lines due to the *trans* form could be weaker than the detection limit.

In recent measurements[16] on clusters of o-fluorophenol with benzene and water the signal arising from clusters of molecules associated with the A band was found to be much stronger than that from clusters associated with the B band. The *trans* isomer is expected to form clusters more easily than the *cis* isomer. So if both excited states have comparable fluorescence lifetimes, the A band should be associated with the *trans* and the B band with the *cis* isomer, respectively.

To decide unambiguously whether the A and B bands arise from the same ground state species, we have applied ground state depletion (hole burning) spectroscopy to

FIG. 1. The two different isomers of *o*-fluorophenol.

FIG. 2. Fluorescence excitation spectrum of *o*-fluorophenol taken by monitoring the fluorescence through a WG 285 (a) and a WG 310 filter (b).

o-fluorophenol. Since the rotational constants of a given state contain much information on the structure of the molecule in that state, we also studied the rotationally resolved ultraviolet excitation spectra of the *A* and *B* band. These spectra enabled us to determine unambiguously the structure of *o*-fluorophenol in both the ground and the excited state.

II. EXPERIMENT

The experimental setup that was used for the low resolution experiments has been described previously.[4] Briefly, the molecules under study are cooled down in a continuous expansion and excited with a frequency-doubled dye laser (Coumarine 540A) pumped by the third harmonic of a YAG Laser (BM Industries or Quantel). The fluorescence is observed at right angle through a WG 285 or WG 310 cut-off filter by a Hamamatsu R2059 photomultiplier. The signal is monitored by a Camac ADC (Lecroy 2249W), connected to a PC.

Lipert and Colson were the first to report hole burning experiments in a supersonic jet.[17] The experiments involve a pump–probe excitation scheme: an intense pump laser beam is scanned through the wavelength region of interest while a counterpropagating probe laser, that is delayed in time, is fixed on a selected resonance. The resulting fluorescence is a measure of the population of the probed ground state level. When both lasers excite transitions which arise from the same ground state species, the pump beam induced depopulation manifests itself by a decrease in the intensity of the fluorescence excited by the probe (spectral hole). If both lasers excite different ground state levels, no spectral hole is observed.

The apparatus that was used to measure the rotationally resolved fluorescence excitation spectra of *o*-fluorophenol has extensively been described elsewhere.[18] A molecular beam was formed by expanding *o*-fluorophenol (Aldrich, 98%), seeded in 0.6 bar argon, through a quartz nozzle with a diameter of about 0.15 mm. The molecular beam was skimmed twice in a differential pumping system and was crossed perpendicularly with a UV laser beam at about 30 cm from the nozzle. The pressure in the detection chamber was below 10^{-6} mbar, assuring collision free conditions. The total undispersed fluorescence was collected by two spherical mirrors and imaged onto a photomultiplier, which was connected to a photon counting system, interfaced with a computer.

Intracavity frequency doubling in a single frequency ring dye laser, operating on Rhodamine 110, was used to generate UV radiation with a bandwidth of 3 MHz. By using a 2 mm thick Brewster cut BBO crystal, 0.15 mW of tunable UV
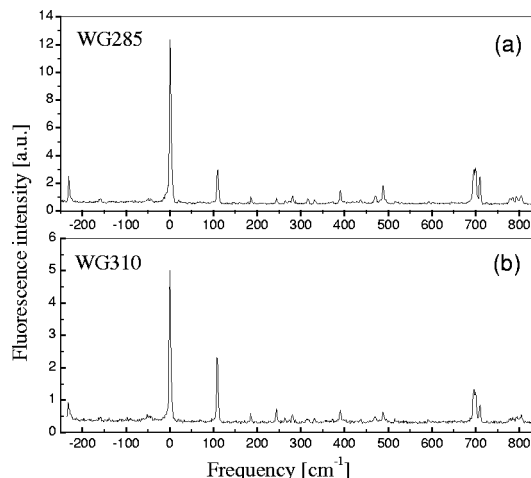
radiation was obtained. A temperature stabilized Fabry–Perot interferometer with a free spectral range of 75 MHz was used for relative frequency calibration, while the iodine absorption spectrum[19] was recorded simultaneously for absolute frequency calibration.

The spectral resolution of the experimental setup is about 16 MHz and is determined by the residual Doppler width in the molecular beam and the geometry of the fluorescence collection optics.

III. RESULTS

A. Low resolution measurements

The fluorescence excitation spectrum of *o*-fluorophenol is shown in Fig. 2(a) (observation through a WG 285 filter) and Fig. 2(b) (observation through a WG 310 filter). The origin,[1] denoted as band *A*, is located at 36 799 cm^{-1} and is followed by a weaker band, located at 109 cm^{-1} (band *B*). The hole burning spectrum, recorded by fixing the probe laser on the *A* band and scanning the pump laser, is shown in Fig. 3 and shows unambiguously that the *A* band and the *B* band are due to the same ground state.
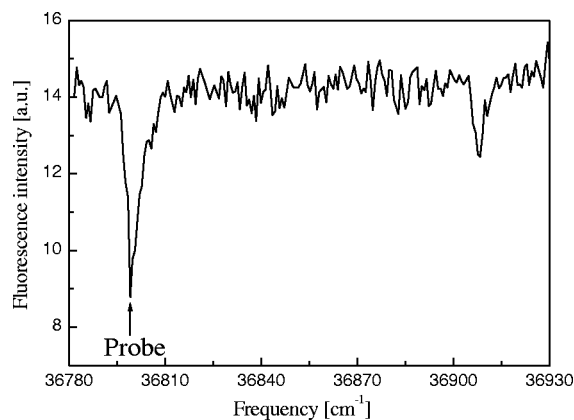
FIG. 3. Hole burning spectrum of *o*-fluorophenol. The probe laser is fixed to the *A* band transition, while the pump laser is scanned over both transitions.
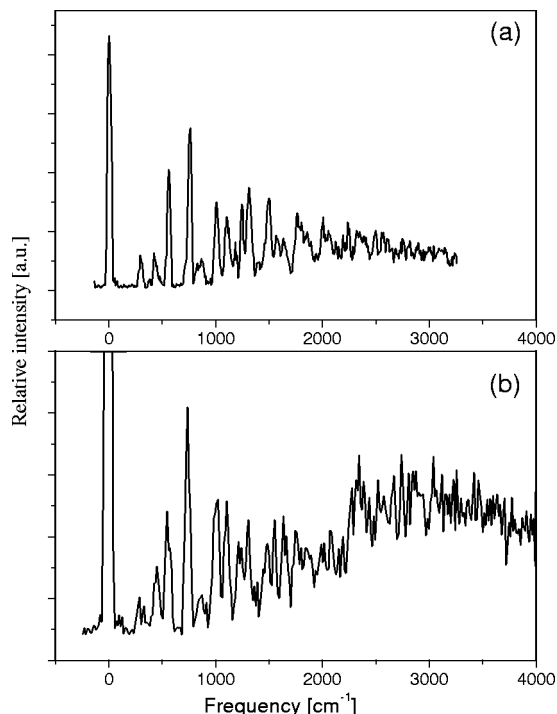
FIG. 4. Comparison of the dispersed fluorescence spectra after exciting the A band at 36 799 cm^{-1} (a) and the B band at 36 907 cm^{-1} (b).

The dispersed fluorescence spectra obtained by exciting the A and B bands are given in Fig. 4. Vibrations that can be assigned to the ring deformation 18a, 6b, and 1 (Wilson's notation[20]), appear in both the excitation and the emission spectra. However, as already noticed by Oikawa et al.,[1] the 109 cm^{-1} frequency has no clear counterpart in the emission spectrum. The emission spectra resulting from excitation of the A and B bands show the same frequencies, i.e., both bands act as origin for the emission spectrum with the lowest frequency mode at 297 cm^{-1}. However, the peak observed around 440 cm^{-1} seems to consist of two transitions at 436 and 468 cm^{-1}, respectively. The latter is much more prominent in the emission spectrum from excitation to the B band.

In addition to the resonant fluorescence that both emission spectra show the B band exhibits a redshifted emission broadened by a spectral congestion, which peaks around 3000 cm^{-1} from excitation. This is confirmed by the excitation spectra recorded through the WG 285 and the WG 310 filter (Fig. 2), which show that the A band emits much more to the blue (resonant emission only) than the B band.

A more careful study of the excitation spectra clearly demonstrates that also the 248 cm^{-1} band displays a redshifted emission. These bands (the B band at 109 cm^{-1} and the 248 cm^{-1} band) are assigned as excitations of the same vibrational mode with a negative anharmonicity. A similar negative anharmonicity was also found for one of the S_1 modes in catechol and its deuterated species.[5,6] In that molecule intense low-frequency vibrations have been observed in both resonance enhanced two-photon ionization and hole burning spectra. For d2-catechol a 105 cm^{-1} mode was found in the $S_0 \rightarrow S_1$ excitation spectrum, while the lowest mode observed in the emission spectrum is at 289 cm^{-1}. This has been explained in terms of a torsion of (one of) the hydroxyl groups, moving in a harmonic potential in the ground state and a double-minimum potential in the electronically excited state. Out-of-plane vibrations were also found in perfluoronaphthol derivatives.[4] The inversion motion of the C–F bonds with respect to the aromatic ring (''butterfly motion'') can also be described by a harmonic potential for the ground state and a double-minimum potential for the excited state.

The lifetimes of both the A and the B band are within the laser pulsewidth. However, the intensity ratio of the two bands in the fluorescence excitation spectrum (~ 2) is smaller than the intensity ratio in the REMPI spectrum (~ 15).[12] This shows that the lifetime of the B band is shorter than that of the A band. The difference in lifetimes cannot be attributed to a difference in the intersystem crossing efficiency, because no difference in the laser induced fluorescence spectrum and the sensitized phosphorescence spectrum has been observed.[2]
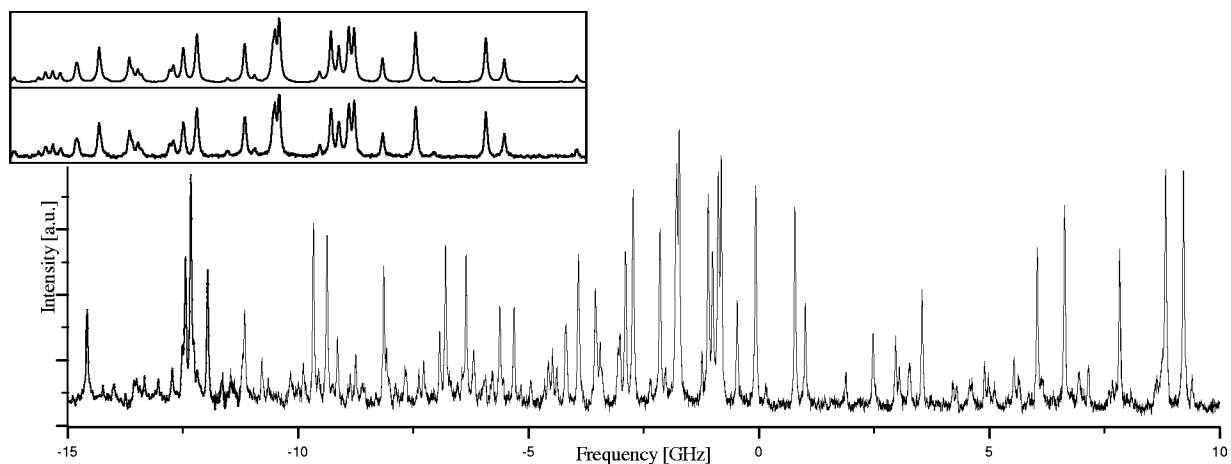

FIG. 5. High resolution spectrum of the A band of o-fluorophenol. The origin (0 on the scale of the figure) is located at 36 799.382(6) cm^{-1}. The inset shows the Q-branch of the spectrum, together with a simulation of this part.
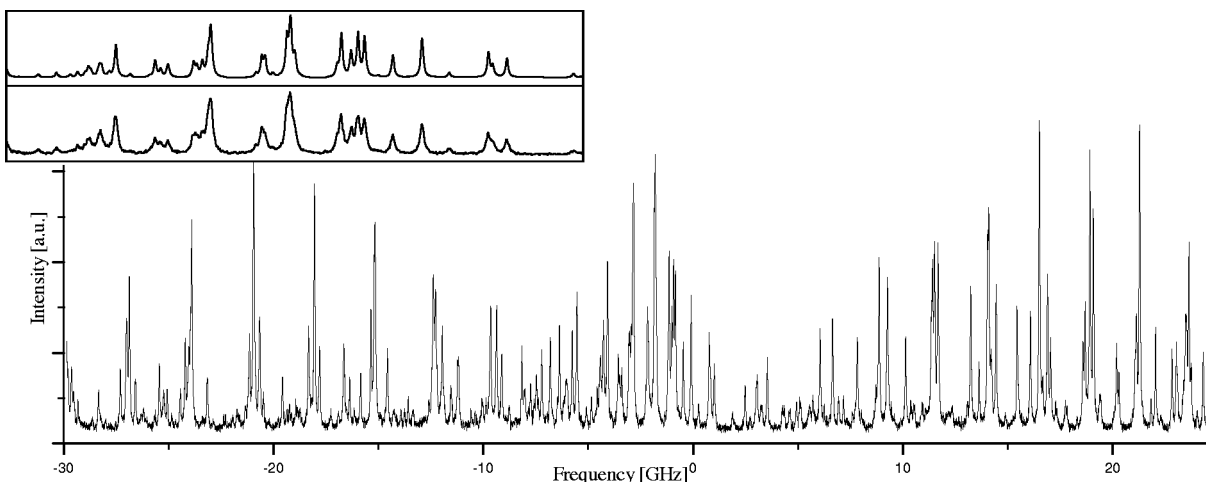
FIG. 6. High resolution spectrum of the *B* band of *o*-fluorophenol. The origin (0 on the scale of the figure) is located at 36 906.710(8) cm^{-1}. The inset shows the *Q* branch of the spectrum, together with a simulation of this part.

B. High resolution measurements

The rotationally resolved UV spectrum of the *A* band of *o*-fluorophenol is given in Fig. 5. It is a *ab*-hybrid type spectrum with its origin situated at 36 799.382 cm^{-1}.

The rotationally resolved UV spectrum of the *B* band is given in Fig. 6. This is also a *ab*-hybrid type spectrum with its origin situated at 36 906.710 cm^{-1}. The lines in the latter spectrum are broader than those in the *A* band transition, indicating a shorter lifetime. An estimation of the lifetimes will be given below.

The analysis of the measured spectra was started with a Gaussian94[21] calculation (using a Becke3LYP functional with the gen basis) of the rotational constants for the ground state of both the *cis* and *trans* isomer. The two sets of calculated rotational constants were used to simulate two spectra from the asymmetric top rigid rotor Hamiltonian. The simulated spectra were compared with the two measured transitions. For both spectra a first assignment was made for some of the lines, which was used as input to a frequency fitting procedure. The ground state rotational constants that resulted from the fits of both transitions were closer to the rotational constants of the *cis* isomer than to those calculated for the *trans* isomer. The difference between the ground state rotational constants of the two transitions was much smaller than the calculated difference between the rotational constants of the *cis* and *trans* isomer. This made us decide to record the hole-burning spectrum described in the preceding section. The result of these measurements clearly indicated that both bands indeed originate from the same ground state.

By improving the fits of both spectra all rotational lines could eventually be assigned with the result that the rotational constants for the ground state were, within their errors, identical to the ground state rotational constants of the *cis* isomer, as determined by microwave spectroscopy.[15] In the next step we performed new fits of our data, fixing the ground state rotational constants to the microwave data of the *cis* isomer. This yielded more accurate constants for the excited state. The results of these fits are given in Table I.

Keeping the rotational constants from the frequency fit fixed, several parameters that determine the intensities of the individual lines were varied in an intensity fit. The population distribution was described by three parameters T_1, T_2, and w in a two-temperature model, where w is the weighting factor for the second temperature:[22,23]

$$n(T_1,T_2,w)=e^{-E/kT_1}+we^{-E/kT_2}. \tag{1}$$

Other parameters that were determined in the intensity fit are the transition moment angle θ_{TM}, that determines the intensity ratio between the *a*- and *b*-type lines, and the Lorentzian contribution to the linewidth $\Delta\nu_L$. The Gaussian contribution to the linewidth was fixed to 16 MHz, the spectral resolution of the experimental setup. The results of the intensity fits are added in Table I.

From the Lorentzian contribution to the linewidth the lifetimes can be estimated. We found 4.6 ± 0.2 ns and 2.8 ± 0.1 ns for the excited *A* state and *B* state, respectively. This is in agreement with the preceding section, where it was concluded that the lifetime of the *B* state is shorter than that of the *A* state. To our knowledge no lifetimes have been reported before for these states.

TABLE I. Molecular constants of *o*-fluorophenol in its ground, excited *A* and excited *B* state. For the ground state the rotational constants A'', B'', and C'' are given, while for the excited states the differences $\Delta A=A'-A''$, $\Delta B=B'-B''$, and $\Delta C=C'-C''$, with the ground state values are given.

	S_0 state[a]	*A* state	*B* state	
A	3337.86(2)	−106.065(10)	−110.915(11)	MHz
B	2231.92(1)	−24.00(5)	−20.684(15)	MHz
C	1337.52(1)	−23.55(3)	−16.492(4)	MHz
θ_{TM}		±23.4(4)	±21.74(13)	degree
ν_0		36799.382(6)	36906.710(8)	cm^{-1}
ΔI[b]	0.008(3)	−0.65(1)	−2.597(4)	amu Å^2

[a]From Ref. 15.
[b]Inertial defect: $\Delta I=I_c-I_b-I_a$, with I_a, I_b, and I_c the moments of inertia along the *a*, *b* and *c* axis, respectively.

IV. DISCUSSION

A. Structural information deduced from the high resolution measurements

As can be seen from the inertial defect, the *cis* isomer is planar in its ground state. The inertial defect is even smaller than that of phenol in its ground state ($\Delta I'' = -0.0309$ amu Å^2),[24] which might be a result of the intramolecular hydrogen bond between the hydroxyl-group and the fluorine atom keeping the hydrogen atom in plane. Evidence for this hydrogen bond is also found if we consider the OH···F distance determined from electron diffraction studies.[25] The OH group is pulled towards the F atom, which results in an OH···F distance that is shorter than the sum of their van der Waals radii.

An increase of the nonplanarity upon electronic excitation was already found for phenol.[24] However, while the inertial defect of the S_1 state of phenol is only -0.18 amu Å^2, in o-fluorophenol it is much larger: -0.65 amu Å^2. A large change like that is quite unusual for aromatic derivatives and it clearly indicates that the molecule is nonplanar in the S_1 state. An even larger inertial defect in the B band (-2.6 amu Å^2) yields unambiguous confirmation that an out-of-plane vibration is involved.

Also catechol is found to be nonplanar in the excited electronic state.[5–7] In that molecule the free OH group rotates over 24° out of the aromatic plane.[7] Nonplanarity of the electronically excited state seems to be a general propensity of fluorinated aromatic species. A coupling between the excited $\pi\pi^*$ state and a $\pi\sigma^*$ state, localized on the C–F bond, has been observed in fluorinated naphthalene derivatives,[4,26] in tetrafluorobenzene[27] and in difluorobenzene[28,29] and has been shown to lead to out-of-plane distortion of the excited state. The latter results in activity of an out-of-plane vibration. In tetrafluorobenzene and the fluorinated naphthalene derivatives this vibration has been identified as the so-called butterfly mode. The nonplanarity of the S_1 state in o-fluorophenol most likely also originates from a coupling between the S_1 state and a $\pi\sigma^*$ state, localized on the C–F bond.

There are several ways in which the ground state structure of o-fluorophenol can be modified so that the rotational constants and inertial defect of the vibrationless S_1 state are reproduced. The first possibility that comes to mind is rotation of the hydroxyl-group around the C–O axis, resulting in an out-of-plane position of the hydrogen atom. A rotation of the OH group over 30° results in a inertial defect of -0.42 amu Å^2. In catechol a similar rotation of the free OH group describes its nonplanarity in the S_1 state. The remaining contributions to the inertial defect in o-fluorophenol can be attributed to smaller out-of-plane displacements of the other atoms and hence explain the inertial defect in the A state of o-fluorophenol.

However, quantitative information on the structural changes upon excitation is difficult to obtain. Many possible geometries reproduce the observed rotational constants. Starting from the ground state structure derived from gas-phase electron diffraction by Vajda *et al.*,[25] various excited state structures have been calculated. The rotational con-
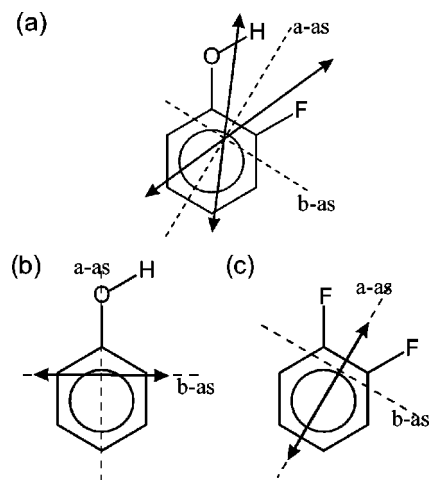

FIG. 7. Direction of the transition moment of the A band of o-fluorophenol ($\pm 23.4°$, determined from the high resolution measurements) (a), compared with the transition moments of phenol (Ref. 24) (b) and di-fluorobenzene (Ref. 29) (c).

stants of the A state could well be reproduced by rotating the hydroxyl group over 30° and, similar to phenol,[22] simultaneously decreasing the C–O and C–F bondlengths and increasing the bonds of the ring. All angles and other bondlengths are kept fixed to the ground state values. The different ring bonds are increased with 0.049 to 0.058 Å (several different combinations are possible), while the C–O and C–F bondlengths are decreased with 0.048 to 0.119 Å. As a result the OH···F distance increases by approximately 0.1 Å, which indicates a weakening of the hydrogen bond. In the ionic state of o-fluorophenol the hydrogen bond is stronger than in the ground state.[12,13] From this one would expect to find a similar strengthening of the intramolecular hydrogen bond in the S_1 state, although somewhat less than for the ion. Possibly, the increase of acidity, that strengthens of the hydrogen bond, has to compete with the out-of-plane distortion, which weakens the hydrogen bond. However, we have to stress here, that the proposed change in structure is not unique and an unambiguously conclusion cannot be drawn on the strength of the hydrogen bond in the electronically excited state.

As mentioned before, the inertial defect of the B state is even larger than that of the A state, and it will require much larger out-of-plane displacements to satisfy this value (-2.6 amu Å^2). The large increase in the inertial defect of the B state gives strong evidence that excitation to this state involves excitation of an out-of-plane vibration.

The directions of the transition moments of the A and B band transition are almost equal, and make an angle of respectively $\pm 23.4°$ and $\pm 21.7°$ with the a axis of the molecule (see Fig. 7). Substitutions are found to be of large influence on the transition moment direction of benzene derivatives. The transition moment of the $S_1 \leftarrow S_0$ transition in phenol lies along the b axis almost perpendicular to the C–O bond.[24] The transition moment of the $S_1 \leftarrow S_0$ transition in o-difluorobenzene is directed along the a axis,[29] which in this case lies in between the two substituted fluorine atoms and intersects the C–C bond perpendicular. Based on these find-
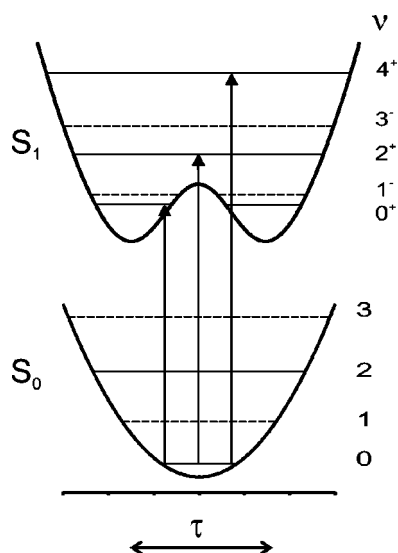
FIG. 8. Harmonic ground state and double-minimum excited state potential along the out-of-plane coordinate τ, together with allowed transitions.

TABLE II. Experimental and calculated vibrational frequencies (cm^{-1}) of the ground state.

Experiment	*Ab initio* Becke3LYP/D95(*d,p*)	Symmetry
	190	a''
	289	a''
297	293	a' (OH$\cdots$F stretch)
	402	a'' (OH torsion)
436	440	a'
468[a]	453	a''
	551	a'
	559	a''
561	577	a' ($6b_1^0$ ring vibration in benzene)
589[a]		τ_2
	707	a''
	755	a''
758	772	a' (1_1^0 ring vibration in benzene)

[a]Most prominent in the emission spectrum resulting from excitation to the *B* band.

ings, we favor the minus sign for the direction of the transition moments in *o*-fluorophenol. This results in a transition moment direction almost parallel to the C–F bond.

B. Out-of-plane deformation

It is concluded in the preceding section that *o*-fluorophenol is nonplanar in the excited state. If we assume that the aromatic ring is still planar, the nonplanarity indicates that there are two equivalent minima on the potential energy surface at either side of the aromatic plane. An out-of-plane rocking motion of the nonplanar group of atoms from one minimum to the other can be described by a double minimum potential along the vibrational coordinate. This is schematically shown in Fig. 8. If we assume that the hydroxyl group dominates the nonplanarity by undergoing a torsional-like motion around the C–O bond, the vibrational coordinate is described by the angle between the hydroxyl group and the aromatic plane. The minima in the double minimum potential will be around 30° above and below the aromatic plane (see Sec. IV A).

The low frequency modes that we have observed in absorption (109 cm^{-1}) and in emission (297 cm^{-1}) behave exactly like the corresponding modes in catechol.[5,6] This is a strong indication that the out-of-plane deformation in *o*-fluorophenol is located on the substituents. Leutwyler and co-workers indeed assigned the 113 cm^{-1} band in catechol to the torsion of (mostly) the hydrogen-bonded OH group. Kleinermanns and co-workers later assigned the 113 cm^{-1} band to the excitation of one quantum of the torsion of the free OH. The hydrogen bond in *o*-fluorophenol is quite weak, as can be inferred from the small displacement of the OH stretching mode relative to phenol (24 cm^{-1}).[12,13] However, it would be surprising that the torsion frequencies of free OH in catechol and bound OH in *o*-fluorophenol are almost identical.

A harmonic ground state potential and a double-minimum excited state potential of the form $V(\tau) = ae^{-2\tau^2}$

$+ b\tau^2 + c\tau^4$ have been fitted to the spectroscopic data for catechol.[5] The C–F butterfly vibrations in the electronically excited states of perfluorinated naphthalene, naphthol,[4,26] and tetrafluorobenzene[27] have also been fitted to such a Gaussian type double-minimum potential.[30] Since the potential in the planar ground state can be described by a single minimum potential, there exists substantial overlap between the ground state and higher vibronic levels in the electronically excited state. Since all out-of-plane motions are of a'' symmetry and both the ground and the electronically excited state are of A' symmetry, only transitions with $\Delta \nu$ is even are allowed. A similar fit to our data can only be performed after it has been established which of the frequencies and overtones belong to the out-of-plane mode. As argued before the excited state 109 cm^{-1} and 248 cm^{-1} frequencies are overtones (τ_0^2 and τ_0^4) of that mode. However, it is difficult to decide which of the ground state frequencies are their counterparts, since both *A* and *B* band seem to behave like origins for the emission spectra. In other words, in emission no clear $\Delta \nu = 0$ transition is observed upon excitation of the τ^2 band. This peculiar distribution of Franck–Condon factors has previously been observed in the butterfly mode of tetrafluorobenzene.[27] After excitation of the 11^2 band the 11_2^2 transition is much weaker in emission than the 11_0^2 transition. This could also be described by a double minimum potential in the electronically excited state.

To further complete the analysis of the ground and excited state frequencies we performed *ab initio* calculations using Gaussian 94.[21] Table II lists the strongest experimental ground state frequencies below 800 cm^{-1}, as well as the calculated frequencies [using a Becke3LYP functional with the D95(*d,p*) basis set]. The observed frequencies are very well reproduced by the calculated a' symmetry vibrations.

Table III displays the measured frequencies in the excited state together with results from CIS/D95(*d,p*) *ab initio* calculations. As common practice for these type of calculations the calculated frequencies are by scaled 0.89. Here no correspondence exists between observed frequencies below 270 cm^{-1} and calculated a' symmetry vibrations. Moreover, the correspondence with a'' symmetry vibrations is also

TABLE III. Experimental and calculated vibrational frequencies (cm^{-1}) in the excited state. Calculated frequencies are scaled by 0.89.

Experiment	Ab initio CIS/D95(d,p)	Symmetry
	74	a''
109		τ_0^2
	152	a''
186		
248		τ_0^4
283	285	a' (OH···F stretch)
	296	a''
	345	a''
389	386	a'
	418	a'' (OH torsion)
	475	a''
486	479	a' ($6b_0^1$ ring vibration in benzene)
	500	a''
	503	a'
	573	a''
	692	a''
697		
700		
725	716	a' (1_0^1 ring vibration in benzene)

poor. This is not at all surprising if any of these frequencies belong to an out-of-plane double-minimum vibration, since in that case we observe the overtones, τ_0^2, τ_0^4, etc., with a negative anharmonicity.

The lowest calculated modes in the excited electronic state are at 74 cm^{-1} and 151 cm^{-1}. The relative motion of the atoms for these vibrations is given in Fig. 9. The 74 cm^{-1} mode corresponds to the 289 cm^{-1} mode in the ground state, while the 151 cm^{-1} mode corresponds to the 190 cm^{-1} ground state mode. In the dispersed spectra we expect to observe the overtone τ_2, which, if one of two above-mentioned vibrations is involved, is predicted around 580 cm^{-1} or 280 cm^{-1}, respectively.

There are several candidates in the emission spectra that can be assigned to the overtone τ_2. The mode at 297 cm^{-1} shows up in the emission spectra originating from both the A and the B band. The most likely assignment for this mode is the totally symmetric OH···F stretching mode, calculated at 293 cm^{-1}. Another possible candidate is the 468 cm^{-1} transition that is observed in the emission spectrum of the B band. This mode would correspond to a harmonic vibration of 234 cm^{-1} in the ground state. However, no vibration is calculated around this frequency. A mode around 580 cm^{-1}
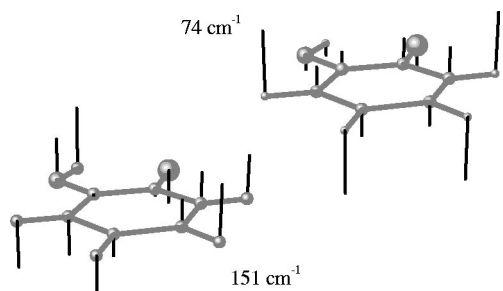

FIG. 9. The two lowest frequency vibrations of o-fluorophenol in the excited state as calculated by Gaussian94 (Ref. 21), using a CIS functional.

would be very close to the totally symmetric ring vibration (6b), observed at 561 cm^{-1} in the emission spectra. Nevertheless, a shoulder seems to appear at the high frequency side of this transition in the emission spectrum of the B band. This might be attributed to the overtone τ_2.

A large redshift of the active out-of-plane vibration upon electronic excitation was found in catechol,[5] perfluoronaphthalene,[26] tetrafluorobenzene[27] and perfluoronaphthol.[4] The 74 cm^{-1} mode (289 cm^{-1} in the ground state) therefore is the most likely candidate for the observed out-of-plane vibration in o-fluorophenol.

A more striking feature in the emissive properties of o-fluorophenol is a clear redshift in the fluorescence after excitation of the overtones of the torsion modes at 109 and 248 cm^{-1}. Besides the narrow bands located near the origin, there exists a broad fluorescence maximum, peaking at 3000 cm^{-1} from the excitation. Such a redshift has been observed before in compounds that contain a OH and a F substituent in ortho position, like perfluorophenols[4] and 2,6-difluorophenol.[6] It should be noted that in the latter case the redshift is even more prominent than in o-fluorophenol. This redshift is thus related to the presence of the interaction between a fluorine atom and an adjacent OH group. Since, in contrast to the ground state, the molecule is not planar in the excited state, the principal axes change upon excitation. The excited state modes are therefore described as a ''mixture'' of ground state modes (Duschinsky effect). The large redshift in an out-of-plane mode upon electronic excitation is most likely due to the presence of high frequency modes in the emission spectrum. These modes gain activity through the Duschinsky effect and have strongly displaced Franck–Condon factors caused by the difference in geometry between the planar ground and nonplanar excited state.

Isotope studies of the molecule would be of great help to determine, firstly, which group of atoms is responsible for the out-of-plane motion, and secondly, which of the remaining frequencies can be attributed to this out-of-plane motion. However, attempts to perform these measurements have failed so far.

V. SUMMARY

The transitions A and B of o-fluorophenol, studied by hole burning spectroscopy and rotationally resolved UV spectroscopy, both originate in the ground state of the cis isomer. The ground state is found to be planar, while it is clearly established that the S_1 state is nonplanar. The inertial defect of the B state is four times that of the A state. The nonplanarity of the S_1 state induces the activity of an out-of-plane vibration, which shows some similarity to the so-called ''butterfly'' mode observed in other benzene derivatives. In the ground state this mode is harmonic, while in the S_1 state it is described by a double-minimum potential with a negative anharmonicity in the vibrational progression. The overtone of this vibration, τ_0^2, is responsible for the strong B band at 109 cm^{-1} to the blue of the $S_1 \leftarrow S_0$ origin.

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