Stark Effects in Gas-Phase Electronic Spectra. Dipole Moment of Aniline in Its Excited S_1 State

T. M. Korter, D. R. Borst, C. J. Butler, and D. W. Pratt*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received June 13, 2000

Abstract: Measurements of the Stark effect on the rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectrum of aniline are reported, providing quantitative information about the degree of charge transfer in the electronic transition. We find that $\mu_a(S_1) = 2.801 \pm 0.007$ D, a value that is ~150% larger than the ground state, $\mu_a(S_0) = 1.129 \pm 0.005$ D. The enhanced value of the dipole moment in the S_1 state is attributed to more efficient electron donation by the *quasi*-planar amino group to the aromatic ring.

Introduction

Photoinduced changes in a permanent electric dipole moment reflect the degree of charge separation for an electronic transition, a quantity of interest in a number of fields, from isolated molecules in the gas phase and in solution, to the band structures of semiconductors and crystalline materials, to complex biological systems.[1] Freeman and Klemperer[2] were the first to determine the excited-state dipole moment of an isolated polyatomic molecule, formaldehyde. Subsequently, Lombardi[3] succeeded in measuring the excited state dipole moments of a number of substituted benzenes by Stark-effect studies of their incompletely resolved UV absorption spectra. Hochstrasser and co-workers[4] performed analogous experiments on larger, oriented molecules in single-crystal hosts. Estimates of excited-state dipole moments also can be inferred using electric dichroism methods in the condensed phase.[5] And, more recently, Hese and co-workers[6,7] have used high-resolution Stark-effect methods to determine the electric dipole moments and polarizabilities of the excited states of large polyatomic molecules in the gas phase. Even relatively low electric field strength experiments on molecules possessing small dipole moments produce measurable splittings in a completely resolved spectrum.

We report here on the application of similar techniques to aniline in its electronically excited S_1 state. It is generally accepted that the ground-state dipole moment of aniline [$\mu(S_0)$] is of order 1 D,[8] with its negative end pointing away from the nitrogen atom toward the aromatic ring. The μ_a component (*i.e.*, the projection of μ along the *a* inertial axis) has been determined to be $\mu_a = 1.129 \pm 0.005$ D in the 0^+ vibrational level of the S_0 state by the microwave measurements of Lister *et al*.[9] Lombardi[10] determined the value $|\Delta\mu_a| = 0.85 \pm 0.15$ D for excitation of aniline to its S_1 state and argued that the sign of $\Delta\mu_a$ is positive, yielding $\mu_a(S_1) = 1.98 \pm 0.15$ D. Later, electric field induced perturbations were observed in the 0_0^0 band of the $S_1 \leftarrow S_0$ spectrum, from which it was concluded that $\mu_a(S_1) = 2.45 \pm 0.10$ D and that the perturbing state, lying within 0.1 cm^{-1}, has a dipole moment of 6.0 ± 0.4 D.[11]

Knowledge of the excited state dipole moment of aniline is important given its ubiquitous role in a wide variety of light-induced charge transfer reactions. An analysis of its fully resolved $S_1 \leftarrow S_0$ electronic spectrum has previously appeared.[12] In the present work, we describe a Stark-effect study of this spectrum using a newly constructed electric field cell, discuss our methods of analysis of the data, and report a refined value of the dipole moment of the isolated molecule in its excited S_1 state. The results are considerably different from those of Lombardi.[10,11] Beyond this, since we also determine from our eigenstate resolved spectra the rotational constants of the S_0 and S_1 states, a connection is established between changes in the charge distribution of the molecule and the changes in its structure that are produced by the absorption of light.

Experimental Section

Aniline was purchased from Aldrich (99%) and used as received. Dry argon gas (99.999%) was used in all experiments.

High-resolution data were obtained using the molecular beam laser spectrometer described in detail elsewhere.[13] The apparatus has been modified to generate a homogeneous, static electric field in the laser/molecule interaction region for the Stark-effect measurements. Briefly, the experiment was as follows. The molecular beam was formed by expansion of aniline vapor (heated to ~365 K) seeded in Ar carrier gas (~500 Torr) through a heated 150 μm quartz nozzle into a differentially pumped vacuum system. The expansion was skimmed 2 cm downstream with a 1 mm skimmer and crossed 13 cm further downstream by a continuous wave ring dye laser operating with R590 and intracavity doubled in BBO, yielding 250 μW of ultraviolet radiation. At the intersection of the two beams, spatially selective optics were used to collect the fluorescence.

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10.1021/ja0021262 CCC: $20.00

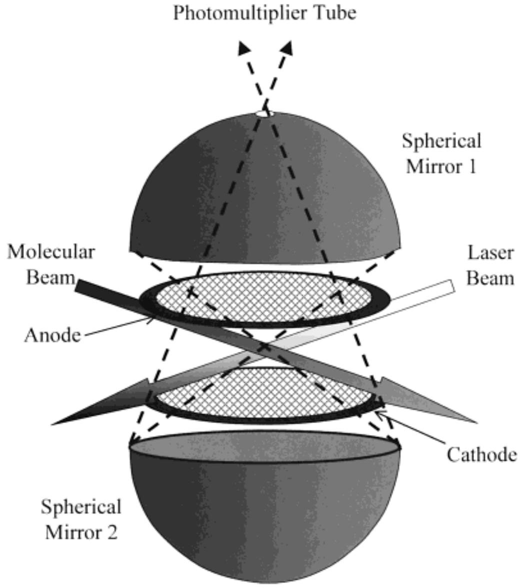

Figure 1. Schematic illustration of the Stark cell. The two electrodes are separated by ~1 cm; the end-to-end separation of the spherical mirrors is 3.5 cm.

Figure 1 shows the new Stark cell. Inside the spherical collecting mirrors, two stainless steel (Type 304) wire grids (diameter = 5 cm, mesh #50, wire diameter = 0.001 in.) were placed one above and one below the laser/molecular beam plane, separated by ~1 cm with ceramic spacers. Two power supplies (Fluke 412 B, 415 B) were used to hold one grid at some positive voltage and the other at some negative voltage relative to a common ground. This experimental setup yields an electric field perpendicular to the polarization of the laser radiation and thus forces a selection rule of $\Delta M = \pm 1$. The collected fluorescence was detected with a photomultiplier tube and photon counting system, and processed by a computerized data acquisition system. Relative frequency calibrations of the spectra were performed using a near-confocal interferometer having a mode-matched FSR of 299.7520 ± 0.0005 MHz at the fundamental frequency of the dye laser. Absolute frequencies in the spectra were determined by comparison to transition frequencies in the I_2 absorption spectrum and are accurate to ±30 MHz.[14] Electric field strengths were calibrated using the known value of μ_a in the ground state of aniline[9] and the combination-difference method of spectral assignment.

Results and Interpretation

Figure 2 shows the rotationally resolved fluorescence excitation spectrum of the 0_0^0 band in the $S_1 \leftarrow S_0$ electronic transition of aniline,[12] recorded in the absence of an electric field. The 0_0^0 band is a *b*-type band with the electronic transition dipole moment oriented along the short in-plane axis (rotational selection rules $\Delta J = 0, \pm 1$; $\Delta K_a = \pm 1$; $\Delta K_c = \pm 1$). It exhibits more than 300 distinguishable rovibronic transitions, with Voigt line shape profiles and line widths (fwhm) of 30 MHz. The homogeneous width of each line is 22 MHz; the excess width of the lines in Figure 2 is due to residual Doppler broadening.

Application of a static electric field to the sample greatly increases the number of transitions in the high-resolution spectrum. Figure 3 shows a typical example from the R branch. The three strongest lines in this region of the zero-field spectrum are (in order of increasing frequency) $|J'\,K_a'\,K_c'\rangle \leftarrow |J''\,K_a''\,K_c''\rangle = |441\rangle \leftarrow |330\rangle$, $|440\rangle \leftarrow |331\rangle$, and $|928\rangle \leftarrow |817\rangle$. Of these, only the first two are significantly influenced by low values of the applied field. These two transitions are each split into several components; a total of 11 such components are resolved at a field strength of 1025 V/cm (not shown). Fourteen components would be expected in a fully resolved spectrum given the selection rule $\Delta M = \pm 1$. The two strongly affected transitions each have the *J* values J', J'' = 4,3 and $|M|$ can take the values 0, 1, ..., J. Levels having the higher values of $|M|$ are most affected by the field and exhibit the larger intensities.

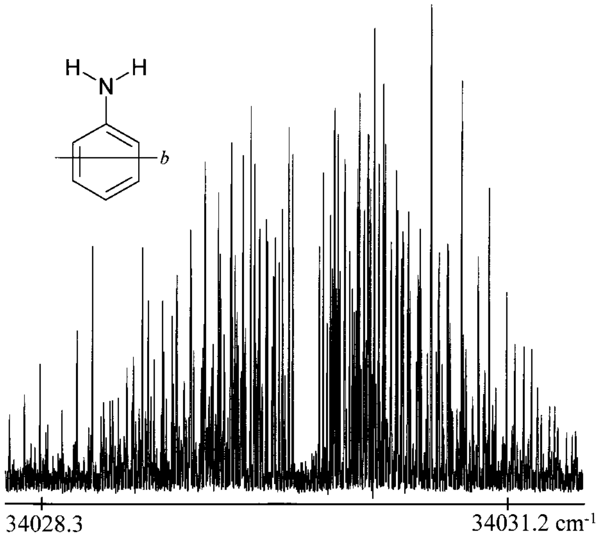

Figure 2. Rotationally resolved fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ origin band of aniline at ~294 nm in the absence of a static electric field.

Figure 4 shows the shifts in transition frequency *vs.* electric field strength for the two resolved Stark-split transitions in Figure 3. The observed tuning curves, while showing remnant second-order behavior at low field strengths, especially for small *M*, are principally first order in character. This is the expected result since both sets of connected rotational levels are es-

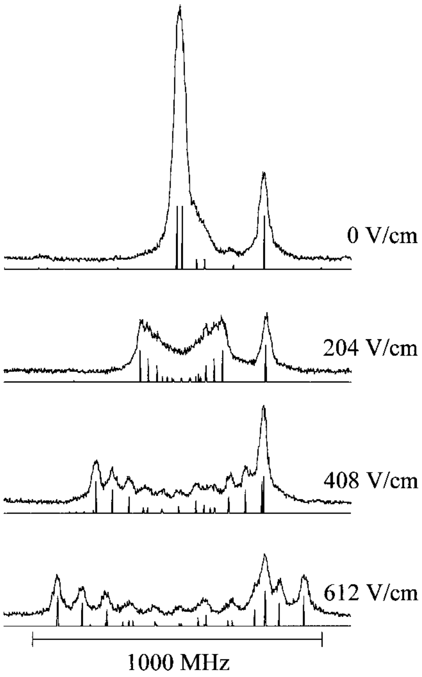

Figure 3. Stark splitting of individual rovibronic transitions in the $S_1 \leftarrow S_0$ origin band of aniline, at different electric field strengths. Each field strength includes two traces. The upper trace is the experimental spectrum and the lower trace is the calculated spectrum. The three strong transitions in the zero-field spectrum are, from left to right, $J'\,K_a'\,K_c' \leftarrow J''\,K_a''\,K_c''$: 441 ← 330, 440 ← 331, and 928 ← 817.

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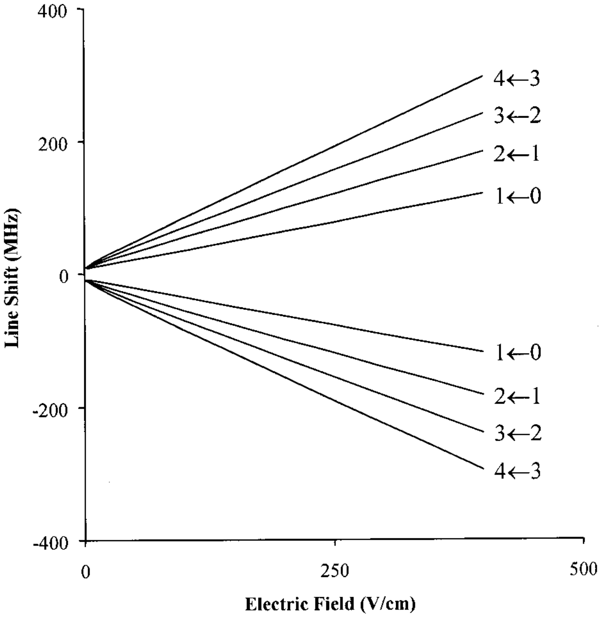

Figure 4. Calculated electric field tuning curves of the 440 ← 331 (upper) and 441 ← 330 (lower) transitions in the $S_1 \leftarrow S_0$ origin band of aniline. Numbers designate the M′ ← M″ values of each transition.

sentially symmetric top levels with $K_a \approx J$. But other transitions exhibit more complicated behavior. Aniline is, after all, an asymmetric top in both of its electronic states ($\kappa(S_0) = -0.575$ and $\kappa(S_1) = -0.505$).[12]

We seek to determine well-defined values of the permanent dipole moment in both electronic states. Hence, we chose to analyze the electric field tuning behavior of *all* resolved lines in the spectrum, not just selected ones. Perturbation theory is inadequate to this task. Therefore, we performed exact diagonalizations of truncated matrices to fit our spectra. The Hamiltonian is

$$\mathbf{H} = \mathbf{H}_r + \mathbf{H}_e \tag{1}$$

where $\mathbf{H}_r$ is the rigid-rotor Hamiltonian,

$$\mathbf{H}_r = AJ_a^{\ 2} + BJ_b^{\ 2} + CJ_c^{\ 2} \tag{2}$$

and $\mathbf{H}_e$ is the Stark Hamiltonian,

$$\mathbf{H}_e = -\underline{\mu}\cdot\underline{E} = -E_Z \sum_{g=a,b,c} \mu_g \phi_{Z_g} \tag{3}$$

Here, A, B, and C are the rotational constants; $J_a^{\ 2}$, $J_b^{\ 2}$, and $J_c^{\ 2}$ are the projections (squared) of the total rotational angular momentum on the inertial axes; E_Z is the applied electric field; μ_g ($g = a, b, c$) are the projections of μ on the inertial axes, and ϕ_{Z_g} are the relevent direction cosines. In a basis of symmetric top functions $|JKM\rangle$, $\mathbf{H}_r$ is diagonal in J and M but nondiagonal in K, making it easily separable into different matrices for each value of J, of size $2J + 1$. By choosing the space-fixed axis Z to be the electric field axis, $\mathbf{H}_e$ is diagonal in M but nondiagonal in J and K; a given J is connected to adjacent $J \pm 1$ blocks in the infinite energy matrix. Thus, to fit our spectra we diagonalized a matrix of elements for $J - 1$, J, and $J + 1$ (of dimension $6J + 3$) for each value of J, and then extracted the relevant eigenvalues and eigenvectors, discarding those corresponding to the $J - 1$ and $J + 1$ blocks, for each electronic state. Then, we calculated the transition frequencies and intensities between the two states as a function of electric field strength, assuming *b*-type selection rules, compared the calculated spectra to the observed ones, and determined the values of the different dipole moment components in the two electronic states by a least-squares fit. Figure 3 shows a typical example that demonstrates the quality of our fits. Increasing the size of the energy matrix by inclusion of $J - 2$ and $J + 2$ terms changes the transition frequencies by only $\sim 10^{-4}$ MHz.

In the case of large field strengths and/or large dipole moments, the J mixing brought about by the electric field can lead to avoided crossings, a breakdown of the $\Delta J = \pm 1$ selection rule, and the appearance of Raman-like $\Delta J = \pm 2$ transitions. As pointed out by Lombardi,[15] these transitions can be thought of as two-photon transitions, where one of the photons is the energy of the dc electric field. Such transitions are weak at the field strengths used here and are ignored. We also neglect higher order polarizability effects.

Accurate determinations of the values of the dipole moment components require accurate measurements of the electric field strength. In the present work, we used the known value of $\mu_a = 1.129$ D[9] for aniline in the 0^+ level of its S_0 state and the combination-difference method to calibrate our Stark cell. An effective field strength of 1018 ± 4 V/cm was found from a combination-difference fit of 74 levels in the S_0 state to the 1000 V/cm spectrum, with a standard deviation of 3.01 MHz, approximately 1/10 of the line width. Thus, the effective spacing of the two electrodes, nominally separated by 1 cm, is 0.982 ± 0.004 cm. All spectra examined using this method yielded the same electrode spacing within one standard deviation.

The electric field tuning behavior of a specific transition in an electronic spectrum depends on the values of all three dipole moment components, in both electronic states. As in microwave spectroscopy,[16] μ_a connects states having $\Delta K_a = 0, \pm 2, ...$ and $\Delta K_c = \pm 1, \pm 3, ...$; μ_b connects states having $\Delta K_a = \pm 1, \pm 3, ...$ and $\Delta K_c = \pm 1, \pm 3, ...$; and μ_c connects states having $\Delta K_a = \pm 1, \pm 3, ...$ and $\Delta K_c = 0, \pm 2, ...$ But the sensitivity of the UV experiment to the different permanent dipole components also depends on the orientation of the electronic transition moment. In the case of the 0_0^0 band of the $S_1 \leftarrow S_0$ transition of aniline, which is *b*-type, the strong $K_a = J$ transitions in the wings of the P and R branches are most sensitive to μ_a, whereas the strong $K_a = 0$ transitions scattered throughout the spectrum are most sensitive to μ_c. Both types of transitions are also sensitive to μ_b, but to a much smaller extent. And, in general, Q branch transitions are most sensitive to the differences in μ_a, μ_b, and μ_c in the two electronic states.

These differences in sensitivity have been exploited in our analysis of the Stark effect on the rotationally resolved $S_1 \leftarrow S_0$ spectrum of aniline. We find that $\mu_a(S_1) = 2.801 \pm 0.007$ D based on a fit of 189 assigned lines with an OMC of 2.45 MHz, again significantly less than the line width. Since $\mu_a(S_0) = 1.129$ D,[9] this means that $\Delta\mu_a = 1.672 \pm 0.007$ D, substantially larger than reported by Lombardi.[10,11] We also find that both μ_b and μ_c are zero in both electronic states within experimental error (0.01 D), since inclusion of either component in either or both states did not improve the fits of the observed spectra. This is consistent with the results of Lister *et al.*,[9] who did not detect any *b*- or *c*-type transitions in their microwave spectra. And, finally, we find no evidence for any field-induced perturbations in our UV spectra. This finding is not necessarily inconsistent with that of Lombardi[11] since his experiments were performed at significantly higher field strengths.

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Discussion

Our refined measurement of the dipole moment of aniline in its S_1 state provides a quantitative measure of the degree of charge separation that accompanies the $S_1 \leftarrow S_0$ transition. We find $\mu_a(S_1) = 2.801$ D, an increase of ~150% compared to the corresponding value in the ground state ($\mu_a(S_0) = 1.129$ D[9]). A substantial amount of charge is moved from the nitrogen atom into the ring when the photon is absorbed, which clearly accounts for aniline's role in a variety of light-induced charge-transfer reactions.

We also find $\mu_b = 0$ and $\mu_c = 0$ in both electronic states of the isolated molecule. Now, the values $\mu_b = 0$ are expected because the molecule has a vertical plane of symmetry perpendicular to the ring. But the values $\mu_c = 0$ are unexpected. Aniline is a nonplanar molecule in its S_0 state, with a dihedral angle of ~38°, and a *quasi*-planar molecule in its S_1 state.[12] The inversion potential function that best fits the S_1 spectroscopic data is essentially quartic with a near-zero barrier.[17] So nonzero values of μ_c in both states, especially S_0, are expected. We believe that the measured values of zero are a consequence of rapid tunneling motion along the inversion coordinate. The inversion splittings in both states are large compared to their rotational constants.[12] Thus, the molecule penetrates (or crosses) the barrier many times during the course of its rotational motion, reversing the sign of μ_c and averaging it to zero.[18]

Two comparisons provide a useful guide to the mechanism of charge separation in the $S_1 \leftarrow S_0$ transition of aniline. The first is with the measured dipole moment of ammonia, which is $\mu = 1.468$ D in the zero-point level of its S_0 state.[19] This value is similar in magnitude to that of aniline, in its ground state. However, the two dipoles differ in their orientations in the molecular frames. The dipole moment in NH_3 is oriented along the nitrogen lone pair axis, whereas that in aniline has a large component perpendicular to the lone pair axis. This difference in the orientation of the two dipoles may be attributed to conjugation of the nitrogen lone pair electrons with the aromatic π orbitals in aniline. The amino group is, after all, an electron-donating substituent when it is attached to a benzene ring.

The second comparison is with the results of *ab initio* calculations using the 6-31G** basis set.[20] Previously, we have found such calculations to be reliable indicators of structure.[12] The rotational constants of the S_0 state are reproduced to within 0.1% of experiment by the MP2 method, and geometry optimizations using the CIS method also accurately reproduce the changes in rotational constants on S_1 excitation. The absorption of a photon flattens the molecule along the inversion coordinate, expands the aromatic ring, and shortens the CN bond. Thus, such calculations should be reliable indicators of photoinduced changes in electronic structure.

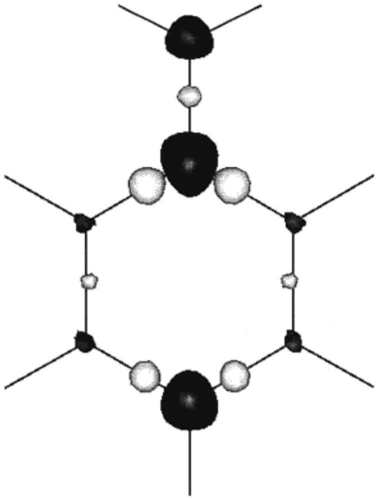

Figure 5. Electron density difference map for the $S_1 \leftarrow S_0$ transition of aniline. Dark contours indicate regions of electron loss, and light contours indicate regions of electron gain.

The value $\mu_a(S_0) = 0.966$ D is found for the MP2 optimized ground state structure, in only fair agreement with experiment. (Theory also gives the values 0.000 and 1.265 D for $\mu_b(S_0)$ and $\mu_c(S_0)$, respectively.) However, the calculations correctly predict the large charge separation that occurs on S_1 excitation. The value $\mu_a(S_1) = 2.867$ D is found for the CIS optimized excited-state structure, in better agreement with experiment. This large increase in μ_a is clearly a consequence of the transfer of charge from the lone pair orbital on nitrogen to the π orbitals of the ring, as shown in Figure 5. Plotted there is the $S_1 - S_0$ difference electron density, computed from the MP2 and CIS wave functions. The nitrogen atom in the S_1 state is clearly electron deficient, compared to that in the S_0 state. Substantial charge reorganization also is observed among the carbon atoms in the ring.

Single-point calculations also were performed on the two theoretical structures. An MP2 calculation on a hypothetical ground-state molecule with a planar amino group yields the value $\mu_a = 1.73$ D, compared to the optimized value of 0.966 D. A CIS calculation on a hypothetical excited-state molecule with a dihedral angle of 38° yields the value $\mu_a = 1.56$ D, compared to the optimized value of 2.867 D. These calculations suggest that it is the orientation of the nitrogen lone pair that is crucial to charge transfer. When the amino group and the benzene ring are coplanar, or nearly so, there is enhanced overlap of the nitrogen lone pair and the ring π cloud, leading to more efficient electron donation by the amino group and increased localization of negative charge on the benzene ring.

Acknowledgment. We thank the machine and electronic shops of the Department of Chemistry, University of Pittsburgh for their valuable contributions to the design and construction of the new Stark cell, R. T. Kroemer, J. W. Ribblett, and M. Schaefer for helpful discussions, and NSF for its financial support (CHE-9987048).

JA0021262

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[18] Even if the tunneling frequency were low, it is likely that a nonzero value of μ_c would have a vanishingly small effect on our spectra at the field strengths employed. This is because μ_c only connects levels that have different symmetries with respect to inversion in the group C_{2v}(M), and because these levels are separated by large energies, ~40 cm^{-1} in the S_0 state and even larger in the S_1 state.[12] Thus, at a field strength of 1 kV/cm, we calculate maximum Stark shifts of order ~100 Hz/D, considerably smaller than the resolution of our experiment.

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