Proton Transfer and Tautomerism in an Excited State of Methyl Salicylate

J. Goodman and L. E. Brus*

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.
Received May 15, 1978

Abstract: Partially resolved vibronic structure has been observed in the fluorescence and excitation spectra of methyl salicylate isolated in solid neon host at 4.2 K. There is no clear spectroscopic evidence for an excited state double minimum proton transfer potential. The applicability of molecular orbital calculations to the keto-enol rearrangement is discussed.

Introduction

Weller has observed that methyl salicylate (methyl 2-hydroxybenzoate) in room temperature aprotic solvents exhibits a simultaneous dual fluorescence.[1-4] One fluorescence band peaking at 3600 Å is simply the mirror image of the lowest near-UV absorption band, while the second fluorescence is strongly red shifted with a maximum near 4400 Å. This second band disappears if the phenolic proton is methylated. Weller proposed that in the excited state a dynamic equilibrium occurs in a proton transfer double minimum potential of the type shown in Figure 1. In the ground electronic state, a strong intramolecular hydrogen bond of the phenolic proton to the carboxylic oxygen occurs.[5] In π-π^* excited states, phenolic groups normally become more acidic and carboxylic groups more basic; therefore an increased interaction is expected. From the temperature dependence of the relative emission intensities, the proton transferred state (producing red-shifted emission) was concluded to lie $\simeq$250 cm^{-1} below the directly produced initial state, which is postulated to give the near-UV fluorescence.

Molecules possessing double minimum potentials are of general interest because of the possibility of information storage at the molecular level, and because of the recent discovery that the initial event in the bovine rhodopsin photochemical mechanism of vision is proton tunneling.[6] Double minimum potentials have been inferred from kinetic data, but to our knowledge have not been directly observed via spectroscopic techniques. One interesting question that could be answered by a spectroscopic potential determination would be identification of the correct reduced mass. That is, as the proton transfers, is a simple dipolar state produced, or is there a compensating readjustment in the remainder of the molecule? In methyl salicylate, the transferred form could be the enol form IIa rather than the dipolar form IIb in Figure 2.[4,7] If IIa is correct, then essentially all the nuclei in the molecule participate in a transition from one minimum to the other. In order to try to answer these questions, we have investigated the fluorescence spectra and the tunable UV laser fluorescence excitation spectra of isolated methyl salicylate molecules in the weekly interacting host solid Ne at 4.2 K.

Weller's postulation of a proton motion double minimum potential is apparently confirmed by molecular orbital calculations of Catalán and co-workers shown in Figure 1.[8,9] If the phenolic proton is allowed two degrees of freedom in the molecular plane, then separate minima near the phenolic and carboxylic oxygens appear in the calculated potential surface for the π-π^* excited state. This same calculation shows only a strong hydrogen bond in the ground electronic state, as experimentally observed. If the Figure 1 barrier height is quantitatively correct, then the Löwdin tunneling formula[10] yields a transfer time for the deuteride of $\sim 10^{-7}$ s. This is readily observable with our nanosecond pulsed UV laser. We shall attempt to observe tunneling by directly exciting the $v' = 0$ state (below the barrier) of the vertical Franck-Condon excited isomer.

Experimental Section

The apparatus has been previously described.[11] We detect time and wavelength resolved fluorescence following pulsed, frequency doubled dye laser excitation of a doped rare gas matrix sample ($\delta\lambda \simeq 0.1$ Å, $\Delta t \simeq 3$ ns). The laser and signal averaging apparatus are controlled by a small computer. The cryostat has two separate gas deposition lines. One line deposits Ne at $\simeq$1.0 mmol/h. The second line contains a U-tube which holds several milliliters of methyl salicylate liquid. Stainless steel bellows valves allow this U-tube to be isolated from the cryostat when not depositing sample, and to be independently pumped to high vacuum without exposing the cryostat to methyl salicylate vapor. During deposition, Ne flows over the thermostated liquid sample at $\simeq$0.1 mmol/h and is deposited.

Liquid methyl salicylate ("oil of wintergreen") is initially purified by repeated fractional recrystallization. In order to eliminate volatile impurities and traces of moisture, the U-tube liquid sample is pumped on under high vacuum ($\simeq 6 \times 10^{-7}$ Torr manifold pressure) for 24 h prior to use. Deuterated methyl salicylate is prepared by adding a 20-fold excess of deuterated methanol to the U-tube liquid, allowing the mixture to stand for several hours, and then pumping at high vacuum for 24 h as before.

Observations

The emission spectrum observed from a methyl salicylate-Ne matrix prepared while thermostating the U-tube at -25 °C appears in Figure 3. A well-resolved origin band appears at 3337 Å, followed to the red by a long progression in a low-frequency $\simeq$190-cm^{-1} mode. This progression ultimately becomes lost in an apparent continuum. Near 3900 Å there is an abrupt increase in the fluorescence intensity, with hints of several vibronic bands in the region 3900–4500 Å. The Franck-Condon maximum occurs near 4400 Å, with a $\simeq$7000 cm^{-1} shift from the origin band. A single lifetime of 12 ± 2 ns is observed at all emission wavelengths without detectable ($\leq$3 ns) rise time. This emission is the red-shifted (proton transferred) fluorescence previously observed by Weller; we do not observe a separate near-UV emission.

These spectra are obtained by excitation at 3231 Å in an excited vibrational level. If one excites in the (0,0) band at 3337 Å, greater resolution is obtained in the vibronic structure near 4300 Å as shown in panel C. If one excites at 2800 Å, which is above the Franck-Condon maximum in absorption, then less structure is observed. In particular, several new sites are observed in fluorescence—both red and blue shifted from the 3337-Å origin.

Part of the apparent lack of structure results from a multitude of sites (the inhomogeneous line width). All attempts to generate better spectra have failed. If the liquid methyl salicylate is thermostated at a lower temperature (-78 °C), thus producing a lower concentration in the matrix, the fluorescence intensity decreases without improvement in spectral quality. Heating the metal deposition line and bellows valve between

0002-7863/78/1500-7472$01.00/0 © 1978 American Chemical Society

EXCITED STATE INTRAMOLECULAR PROTON TRANSER IN SALICYLIC ACID

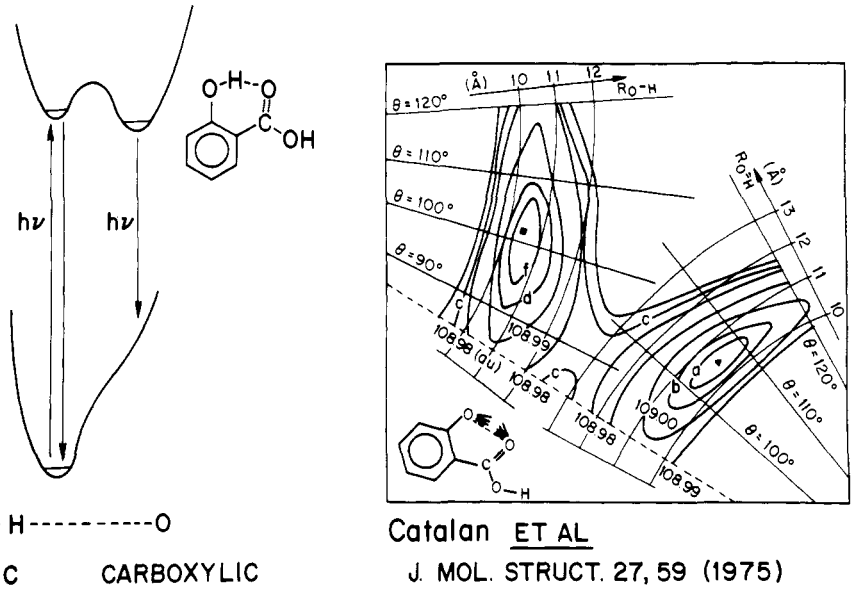

Figure 1. Left-hand side shows schematic proton transfer double minimum potential suggested by Weller. Right-hand side shows calculated π-π^* double minimum potential of Catalan et al. in ref 8 and 9. The proton is allowed two degrees of freedom in the molecular plane.

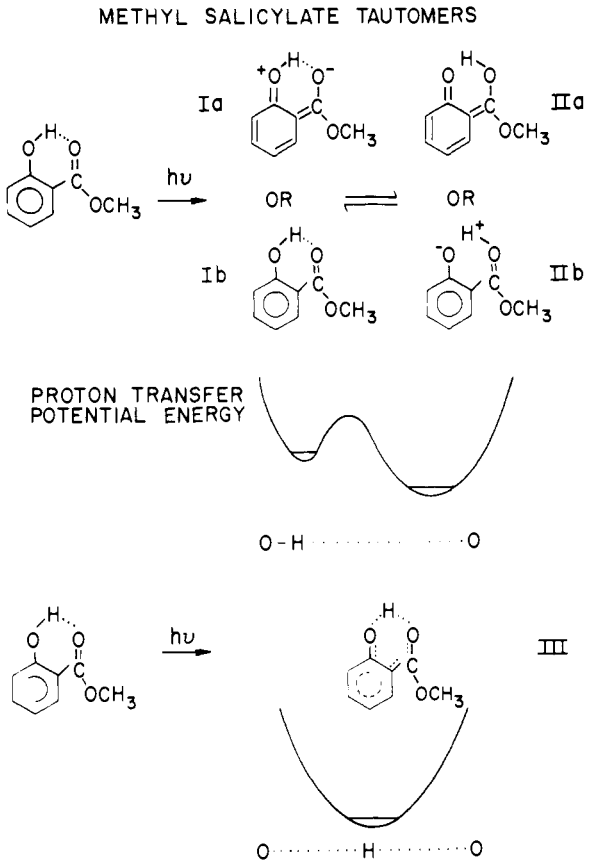

Figure 2. Possible tautomeric forms which may occur in the π-π^* excited state. Ia and Ib represent two limiting cases for the untransferred form, corresponding to the metastable left-hand side minimum in the potential curve. Similarly, IIa and IIb are limiting forms for the proton transferred species corresponding to the right-hand side minimum. III is Rauh's resonance form (ref 12) in which the proton potential has a single minimum midway between the carboxylic and phenolic oxygens.

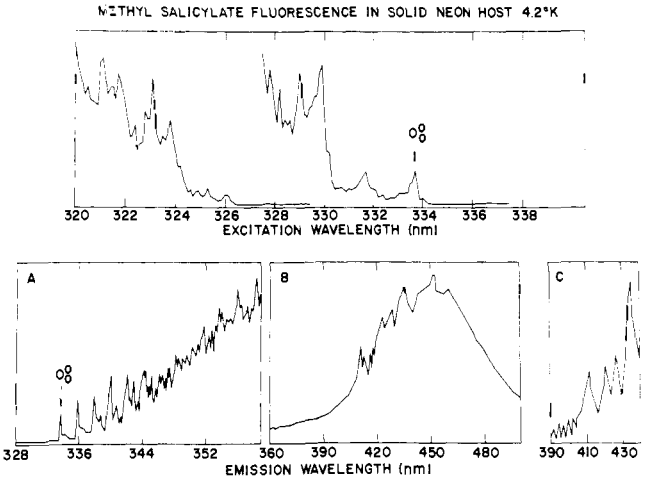

Figure 3. Experimental excitation and emission spectra. Upper panel is a digital excitation spectrum of 4350-Å fluorescence. Individual points, which are 1 Å apart, are connected by straight lines for visualization purposes. Lower panels A and B are digital emission spectra produced by 3231-Å excitation. Individual points, which are again 1 Å apart, have been connected by straight lines. Panel C shows greater resolution of vibronic structure produced by excitation in the O_0^0 origin.

the U-tube and cryostat during deposition produces unchanged spectra. We conclude that the spectra are characteristic of isolated methyl salicylate monomers. Under the supposition that trace amounts of moisture could complicate the spectra, we gave the cryostat an extended bakeout and added molecular sieves to the liquid sample. No spectral improvement occurred.

Nevertheless, the fluorescence excitation spectra, as well as the emission spectra, show reproducible vibronic features. The (0,0) origin is clearly observed at 3337 Å in the Figure 3 excitation spectra. There is a progression of intensity thresholds (3337, 3299, 3260, and 3238 Å) where successive fivefold increases in absorption intensity occur. These appear to be a Franck-Condon progression in an excited-state mode in the 350-cm^{-1} range. The extreme intensity increase for each successive member indicates that a large displacement has occurred along the appropriate normal mode. In addition there

are other progressions of lower frequency 100–200-cm^{-1} modes.

The fluorescence shows no detectable rise time for excitation in any of the low-energy vibronic bands, including the origin band. This origin band necessarily directly produces the proton transferred (fluorescing form) excited state. A possible rise time due to tunneling following excitation of the untransferred form $v' = 0$ level would be orders of magnitude slower in the deuteride. The origin band of the untransferred form would appear as an excited vibronic level in our spectra. We have succeeded in preparing a 60% deuterated methyl salicylate sample as judged by a new origin band which appeared blue shifted at 3327 Å. The combination of both isotopes in the matrix unfortunately produced overlapping emission spectra without apparent vibronic structure. The shape of the Franck–Condon envelope in the range 4000–4500 Å is unchanged. A lifetime of 18 ± 2 ns was observed, without apparent rise time for excitation in any of the low-lying vibronic levels.

In summary, a comparison of our emission spectra with those of Weller indicates that we have unambiguously observed the red-shifted emission originally assigned to the proton transferred excited state. The coincidence of the O_0^0 band in absorption and fluorescence implies that the laser directly excites this isomer for excitation at 3337 Å. This statement assumes that the absorption and fluorescence have the same vibrationless electronic ground state in common.

Discussion

The fact that we have partially resolved vibronic structure allows us to draw conclusions concerning the existence of a double minimum potential. If the excited state were a hydrogen motion double minimum potential with a $\simeq$250-cm^{-1} separation between the two $v' = 0$ levels, then we would expect a different excitation spectrum—even if tunneling from the higher to lower $v' = 0$ level occurs on a subnanosecond time scale. In Figure 1, the Franck–Condon factor for absorption to the untransferred $v' = 0$ state directly above the ground-state $v'' = 0$ should be $\simeq 1.0$. However, the Franck–Condon factor for nonvertical absorption into the lower minimum $v' = 0$ level should be extremely small. If this second minimum is shifted by ~0.7 Å as in the calculation of Catalán, and if we take the two OH vibrational frequencies in the upper state to be $\simeq$1000 cm^{-1}, then a simple model calculation yields a Franck–Condon factor of $\approx$0.003. This implies that a false Franck–Condon origin, 300 times as strong as the true origin band at 3337 Å, should appear in the excitation spectra about 250 cm^{-1} above the true origin. Such a band is not present; we see rather *progressions* of absorption thresholds characteristic of excited state nearly harmonic vibrations.

Thus our spectra do not show the expected structure of a keto–dipolar state (Ib ↔ IIb) double minimum potential. This same argument applies to a keto–enol (Ib ↔ IIa) rearrangement, in which the Franck–Condon factor for $v' = 0$ of the enol form would be even lower owing to additional poor Franck–Condon factors in other modes. If an equilibrium of the form Ia ↔ IIa occurred, then both $v' = 0$ levels would have very low Franck–Condon factors in absorption. However, the IIa Franck–Condon factor would still be lower than the Ia factor by the previously calculated H motion Franck–Condon factor, and thus our spectra also seem to be inconsistent with this type of double minimum potential.

We conclude that we observe no clear evidence for a double minimum potential in which one $v' = 0$ level lies 250 cm^{-1} above another $v' = 0$ level. Rather, the participation of low-frequency modes in absorption and fluorescence, the extremely weak origin band, and the large Stokes shift in emission all argue for a single excited geometry with a very large change in structure from the ground electronic state. The Franck–Condon envelopes are different in absorption and fluorescence. This lack of mirror symmetry cannot come from a simple model of displaced harmonic oscillators in ground and excited states, but instead suggests a scrambling of ground-state normal modes in the excited states.

Our spectra refer to methyl salicylate in Ne host. In this situation the influence of "solvation" on the molecular structure should be considerably less than in previous investigations in aprotic and protic solvents. We cannot experimentally rule out the somewhat unlikely possibility that the two (transferred and untransferred) $v = 0$ states are coincident within $\simeq$10 cm^{-1} in our spectra.

The 4100–4300 Å resolved vibronic structure in fluorescence is shifted 5600–6900 cm^{-1} from the (0,0) band. These bands could be interpreted as populating $v = 2$ of the OH stretch in the ground electronic state, along with several quanta of some other low-frequency mode. It is remarkable that these bands are much stronger than the $v = 1$ and $v = 3$ transitions. This observation again suggests a scrambling of normal modes.

These observations are consistent with the quinoid structure IIa in the excited state; a second possibility also exists. Rauh[12] has performed MO calculations on the keto → enol (Ib → IIa) transformation in the π–π^* excited state under the assumption that the molecule smoothly adjusts from keto to enol form as the proton moves from phenolic to carboxylic oxygen. This calculation shows one potential minimum in the middle of the assumed tautomerism coordinate; that is, with the proton midway between the oxygens as in form III of Figure 2. Our data do not distinguish between this form and the complete quinoid form IIa. We suggest that this extensive reorganization in the molecule lessens the usefulness of molecular orbital calculations in which only the H atom moves.[8,9]

What is the cause of the near-UV fluorescence observed in fluids? Recently Klöpffer and Naundorf[13] and Kosower and Dodiuk[7] have observed that the dual luminescence in alcoholic solvents is a function of excitation wavelength. That is, the excitation spectrum of the near-UV emission is slightly blue shifted with respect to that of the "proton transferred" form. They conclude that two different species in the liquid are excited and separately give rise to the two emissions. In this case the ~250-cm^{-1} splitting would apply to the ground electronic states before excitation. The red-shifted emitter is identified as the enol (IIa) formed by exciting the internally hydrogen-bonded form, while the near-UV emitter is identified as an isomer in which the phenolic proton and carboxylic oxygen are externally hydrogen bonded. While this conclusion seems to be firmly established in alcoholic solvents, it is not clear why the dual emission appears in aprotic solvents, the neat liquid, and in the vapor phase. In these cases it may simply be that at higher temperatures the non-internally hydrogen bonded ground state isomer is slightly populated and excited. At 4.2 K in solid neon, we expect only the lowest energy ground-state isomer, which is undoubtedly the internally hydrogen bonded form, to occur.

References and Notes

(1) A. Weller, *Naturwissenschaften*, **42**, 175 (1955).
(2) A. Weller, *Z. Elektrochem.*, **60**, 1144 (1956).
(3) A. Weller, *Prog. React. Kinet.*, **1**, 188 (1961).
(4) H. Beens, K. H. Grellmann, M. Gurr, and A. Weller, *Discuss. Faraday Soc.*, **39**, 183 (1965).
(5) G. E. Maciel and G. B. Savitski, *J. Phys. Chem.*, **68**, 437 (1964).
(6) K. Peters, M. L. Applebury, and P. M. Rentzepis, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 3119 (1977).
(7) E. M. Kosower and H. Dodiuk, *J. Lumin.*, **11**, 249 (1975).
(8) J. Catalán and J. I. Fernandez-Alonso, *J. Mol. Struct.*, **27**, 59 (1975).
(9) J. Catalán and F. Tomas, *Adv. Mol. Relaxation Processes*, **8**, 87 (1976).
(10) P. O. Löwdin, *Adv. Quantum Chem.*, **2**, 213 (1965).
(11) J. Goodman and L. E. Brus, *J. Chem. Phys.*, **65**, 1156 (1976).
(12) R. D. Rauh, Thesis, Princeton University, 1972.
(13) W. Klöpffer and G. Naundorf, *J. Lumin.*, **8**, 457 (1974).