

TABLE I. Potential energy surface parameters for NN-HF and OC-HF.

Computational level	NN-HF		OC-HF	
	R_e (Å)	D_e (cm ⁻¹)	R_e (Å)	D_e (cm ⁻¹)
DZ/SCF	2.951	1460	3.122	1450
DZ + P/SCF	3.081	737	3.169	1031
TZ + P/SCF	3.186	540	3.211	748
TZ' + P/SCF	3.182	541	3.209	745
DZ + P/SCEP	2.964	1133	3.074	1361
DZ + P/ACCD	2.958	1188	3.076	1372
TZ + P/ACCD	3.069	795	3.098	1066

607 cm⁻¹ for NN-HF and 987 cm⁻¹ for OC-HF which differ by around 100 cm⁻¹ from the TZ + P/ACCD predictions.

The seriousness of basis-set deficiencies and neglect of electron correlation effects leads to certain unique occurrences. For instance, the R_e of the NN-HF complex at the DZ + P/SCF level is within 0.001 Å of the spectroscopically inferred vibrationally-averaged monomer separation value. That this is not some exploitable cancellation of neglected effects is immediately revealed by the OC-HF results where the same comparison gives a huge difference of 0.121 Å. Furthermore, vibrational averaging we have carried out for these systems using a Numerov-Cooley vibrational wave function¹⁷ for a pseudodiatom model of the complexes shows that $R_e - R_0$ differences cover a range of large corrections (0.02–0.05 Å). Therefore, structures, force constants, and one electron properties of these two and perhaps other complexes, when determined with small basis sets and/or the neglect of electron correlation effects, are of questionable value. In the forthcoming report, we shall examine these deficiencies, especially as they pertain to the nature of the weak attraction that leads to complex formation.

The support of the Quantum Chemistry Program of the

National Science Foundation is gratefully acknowledged. The calculations were carried out on the Illinois Theoretical Chemistry Minicomputer System and with time provided by the University of Illinois Research Board.

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Picosecond excitation of jet-cooled hydrogen-bonded systems: Dispersed fluorescence and time-resolved studies of methyl salicylate^{a)}

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(Received 12 May 1982; accepted 1 June 1982)

Picosecond studies of the excited state proton transfer dynamics of molecules in solution^{1–3} and in the gas phase⁴ have received considerable attention. However, no time-resolved work has been reported on such molecules cooled by supersonic jet expansion. Here, we communicate new results on the frequency-dispersed

and picosecond time-resolved fluorescence characteristics of the blue-emitting form of jet-cooled methyl salicylate (MS). These results, when combined with the jet excitation spectra,⁵ provide new information regarding the spectra of the isolated molecule, and its dynamics at different excess vibrational energies.

Jet-Cooled Fluorescence Spectra of MS

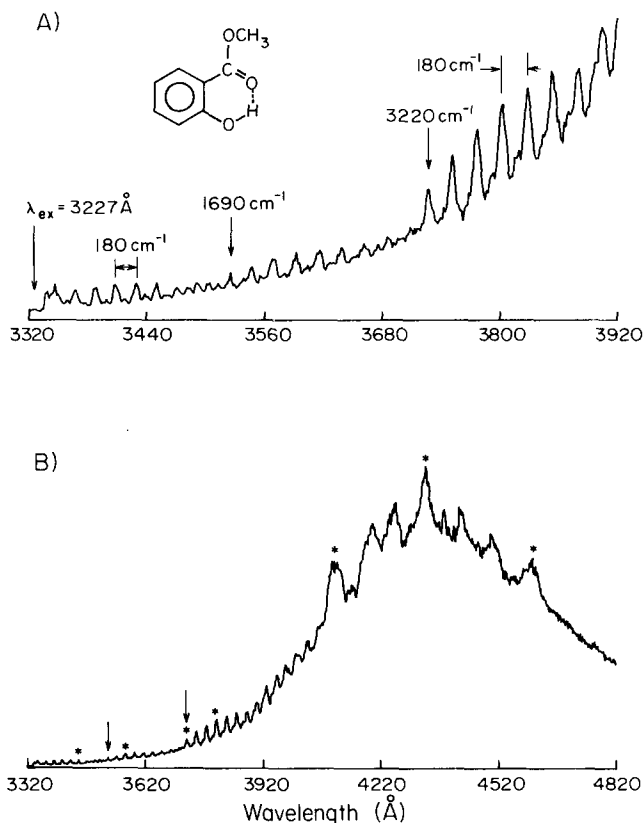


FIG. 1. Dispersed fluorescence of jet-cooled methyl salicylate excited at 3327.5 Å. Conditions were identical for the two spectra: Monochromator resolution = 5 Å, laser-nozzle distance ($\equiv x$) = 1 mm, pinhole diameter ($\equiv D$) \approx 150 μ , 25 psi He, nozzle temperature ($\equiv T$) \approx 70°C. Spectra were found to be unchanged at increased x . Arrows mark the positions of the 1690 and 3220 cm^{-1} bands, and asterisks mark the detection wavelengths at which decays were taken with $x=3$ mm and monochromator resolution = 20 Å.

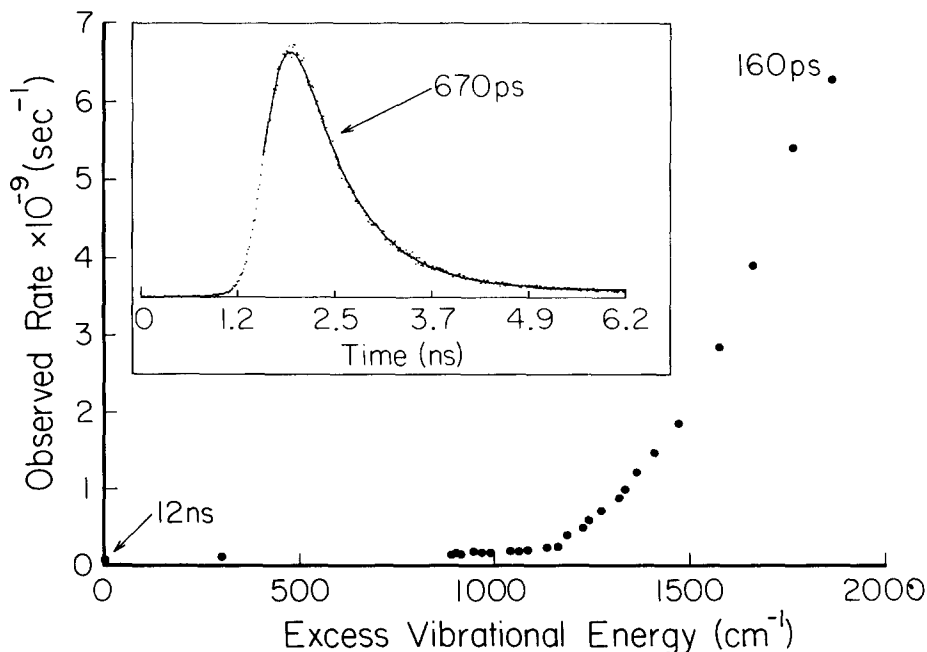


FIG. 2. Fluorescence decay rate of MS vs excess energy. Experimental conditions: Excitation bandwidth = 0.5 Å, monochromator resolution \approx 40 Å, detection wavelength = 4350 Å, $x=2$ mm, $D \approx 50 \mu$, 50 psi He, $T=25^\circ\text{C}$. The inset shows a typical decay and fitted curve corresponding to a point at the high energy end of the plot.

The excitation of MS in the near UV results in a fluorescence component that exhibits an extreme Stokes shift.^{6,7} Experimental evidence points to the conclusion that this blue emission arises from an excited state species, the phenolic hydrogen of which has been displaced towards the carbonyl oxygen.⁷⁻⁹ Although much work^{2-5,7-13} has been done concerning this "blue" form, important questions remain. First, the proper description of the formation of this species is not unambiguously established. Experiments at room temperature in solution,³ and in low-temperature neon matrices¹⁰ have suggested that the absorption of light and the preparation of the blue form occur simultaneously. However, the interpretation of these experiments must take into account solvent interactions and/or thermal energy effects. Second, the nonradiative decay processes are not fully characterized. Emission yields and lifetimes in the gas phase^{4,13} and in solution^{2,3} imply the existence of an efficient radiationless decay channel at high excess energies in the blue species. Again, the presence of solvent, the finite temperature of the sample, or both, introduce complications into the interpretation of the results. Supersonic jet spectroscopy is expected to eliminate these complications due to thermal and solvent effects.

The supersonic cw jet was prepared by expanding 25–50 psi of helium seeded with vacuum-distilled MS (Aldrich, 98%) into an evacuated chamber kept at 10^{-4} Torr. The molecules were excited with ≤ 15 ps pulses obtained by frequency doubling the output of a synchronously-pumped, cavity-dumped dye laser. Fluorescence was collected with right-angle geometry, passed through a monochromator, and detected with a fast photomultiplier. Decays were measured by time-correlated, single-photon counting.

Jet-cooled spectra of MS for 3327.5 Å excitation are presented in Fig. 1. A striking feature is the presence

of long progressions involving frequency intervals of 180 cm^{-1} , which are built on 0, 1690, and 3220 cm^{-1} shifts from the excitation energy. The fluorescence decays of different bands for this excitation energy [see Fig. 1(b)] are well fit by single exponentials and give identical lifetimes of $12 \pm 0.5\text{ ns}$.

As the excitation energy increases, a marked increase in decay rate is observed.¹⁴ As evident from Fig. 2, this increase appears to have a threshold at $\sim 1300\text{ cm}^{-1}$ of excess vibrational energy (i.e., the energy above 3327.5 \AA).

For excitation at 3327.5 \AA in the jet, three observations are pertinent to the characterization of the emitting state. First, fluorescence lifetimes are identical across the fluorescence spectrum. Second, there is no apparent rise time to any of these decays. Third, the fluorescence progression extends from the excitation energy. These results indicate that the distorted excited state is created simultaneously¹⁰ with the absorption of a photon in the isolated molecule. It is likely that the 180 cm^{-1} interval corresponds to a ground-state out-of-plane bending motion of the "ring" that includes the intramolecular hydrogen bond. Progressions of this interval are built on 1690 and 3220 cm^{-1} shifts, the ground state carbonyl and O-H stretches,¹⁵ respectively. The appearance of these modes would be expected given an excited state distortion involving phenolic hydrogen displacement toward the carbonyl.

For higher excitation energies, the marked shortening of the lifetime indicates that an efficient intramolecular decay process exists. The onset of this shortening at $\lambda_{ex} \approx 3200\text{ \AA}$ is consistent with the fall-off of intensity in the jet-cooled excitation spectrum,⁵ which can be linked to a decrease in fluorescence quantum yield. Furthermore, the 1300 cm^{-1} threshold (3.7 kcal/mol) is in excellent agreement with the activation energy for the nonradiative rate derived from studies in solution.³

The marked change in the decay rate (12 ns to 160 ps) presented here, in light of recent time-resolved jet experiments,^{16,17} is suggestive of some pertinent considerations regarding MS radiationless decay. In particular, it is, perhaps, not entirely accidental that the behavior shown in Fig. 2 so closely parallels that of *t*-stilbene.¹⁶ The existence of low frequency torsions and bends, which can promote excited state configuration

change or electronic state coupling, could explain the decay behavior of MS and *t*-stilbene as opposed to the more gradual fall-off in lifetime of more rigid molecules such as anthracene.¹⁷ The involvement of such motions in MS radiationless decay is further supported by the prominence of the 180 cm^{-1} progression, and by the viscosity dependence of the fluorescence lifetime in solution.³ A full account of this work will be published later.

^aThis work was supported by a grant from the National Science Foundation, No. CHE81-12833.

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