

Gas-Phase Inorganic Chemistry: Laser Spectroscopy of Calcium and Strontium Monothiolates and Monohydrosulfides

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The gas-phase reaction of Ca and Sr vapors with various thiols and hydrogen sulfide was studied. These reactions produced the metal monothiolates CaSR and SrSR, where R = H, CH₃, CH₂CH₃, etc. Three electronic transitions, $\tilde{C}^2A'-\tilde{X}^2A'$, $\tilde{B}^2A''-\tilde{X}^2A'$, and $\tilde{A}^2A'-\tilde{X}^2A'$, were detected by laser-induced fluorescence. The spectra are consistent with a bent Ca-S-R structure. Some Ca-S and Sr-S stretching frequencies were determined from the spectra.

Introduction

The interaction of metals with sulfur-containing molecules is an important area in inorganic chemistry.¹ Metal thiolates are often studied because they provide models for naturally occurring sulfur-containing compounds found, for example, in the active sites of proteins. Zn and Cd thiolates have been known for a long time.² These compounds are studied partly because of the biological importance of the elements and partly because zinc dithiocarbamate and related compounds act as accelerators in the vulcanization of rubber by sulfur. Ag(I) and Au(I) thiolates have been extensively studied in relation to chemotherapy for arthritis.³

Although the action of H₂S on metals commonly gives insoluble sulfides, some complexes of H₂S are known, although they are readily oxidized to sulfur or deprotonated to SH⁻ complexes.⁴

There has been no previous experimental work on gas-phase alkaline earth metal monothiolates. The smallest members of the alkaline earth monothiolate family (M-SR, M = Ca, Sr) are the triatomic hydrosulfides CaSH and SrSH. We have previously studied many monovalent derivatives of Ca and Sr in our laboratory, including those with metal-oxygen,⁵⁻⁸ metal-nitrogen,^{9,10} metal-carbon,¹¹⁻¹³ and metal-boron¹⁴ bonds. The observation of calcium and strontium monothiolates extends our work to the next row of the periodic table.

High-resolution analysis proves that alkaline earth monohydroxides are linear.^{5,6,15-17} Recently, the gas-phase calcium and strontium hydrosulfide molecules were studied at high resolution in our laboratory.¹⁸ These high-resolution analyses proved that CaSH and SrSH are bent. Electron propagator calculations by Ortiz¹⁹ confirm that the ground and excited states of CaSH are bent, having C_s symmetry. The optimum calculated geometry for the ground state has a Ca-S bond length of 2.614 Å, a S-H bond length of 1.346 Å, and a Ca-S-H bond angle of 100.0°.

In the experiments reported here, three electronic transitions ($\tilde{A}-\tilde{X}$, $\tilde{B}-\tilde{X}$, and $\tilde{C}-\tilde{X}$) of the gas-phase calcium and strontium thiolates were studied at low resolution. The method of synthesis of these compounds and the analysis of their spectra are discussed.

Experimental Section

The calcium and strontium thiolates were made in a Broida-type oven¹⁸ by the reaction of the electronically excited metal vapor with the appropriate thiol or H₂S, similar to previous work in this area.⁵⁻¹⁸ The Ca or Sr metal was vaporized from a resistively heated crucible, carried to the reaction region by argon carrier gas, and reacted with the oxidant. The total pressure inside the oven was maintained at ≈1.5 Torr, with a few milliTorr of the oxidant. All the thiols used in this study were purchased from the Aldrich Chemical Co. (97% purity). The vapor pressures at room temperature were sufficiently high for the production of thiolates. For H₂S the gas from a lecture bottle (Matheson) was admitted to the oven.

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TABLE I: Band Centers of the Calcium Thiolates (in cm⁻¹)

molecule	$\tilde{A}^2A'-\tilde{X}^2A'$	$\tilde{B}^2A''-\tilde{X}^2A'$	$\tilde{C}^2A'-\tilde{X}^2A'$
CaSH	15 366	15 810	16 082
CaSCH ₃	15 509	15 807	
CaSCH ₂ CH ₃	15 463	15 760	
CaSCH ₂ CH ₂ CH ₃	15 455	15 711 ^b	
CaSCH(CH ₃) ₂	15 423 ^a	15 694 ^b	
CaSC(CH ₃) ₃	15 434 ^a	15 664 ^b	
CaSCH(CH ₃)C ₂ H ₅	15 432 ^a	15 694 ^b	

^a Broad peak. ^b Overlapped with the $\tilde{B}-\tilde{X}$ transition of CaSH.

TABLE II: Band Centers of the Strontium Thiolates (in cm⁻¹)

molecule	$\tilde{A}^2A'-\tilde{X}^2A'$	$\tilde{B}^2A''-\tilde{X}^2A'$	$\tilde{C}^2A'-\tilde{X}^2A'$
SrSH	14 293	14 815	15 026
SrSCH ₃	14 407	14 780	15 468
SrSCH ₂ CH ₃	14 355	14 745	15 499
SrSCH ₂ CH ₂ CH ₃	14 351	14 734	15 466 ^a
SrSCH(CH ₃) ₂	14 329	14 732	
SrSC(CH ₃) ₃	14 318	14 732	
SrSCH(CH ₃)C ₂ H ₅	14 323	14 728	

^a Broad peak.

Two CW broad-band (~1 cm⁻¹) dye lasers pumped by the all lines output of Coherent Innova 90 and Coherent Innova 70 argon

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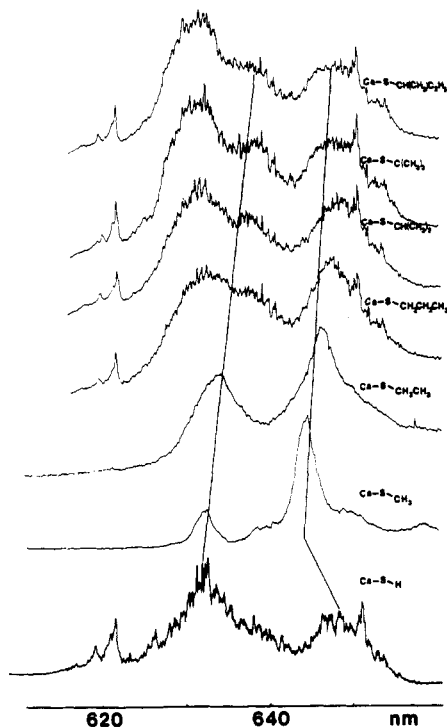


Figure 1. Laser excitation spectra of calcium thiolates. The corresponding transitions for the different thiolates are connected by a line. CaSH is also observed in the spectra of the larger thiolates in the upper four panels. The transitions of these four larger thiolates are badly obscured by the transitions of CaSH.

ion lasers were used in this experiment. The dye lasers were operated with Pyridine 2, DCM, and Rhodamine 6G dyes. One dye laser beam was focused into the oven to probe the molecular transition. The second dye laser was used to excite the alkaline earth $^3P_1-^1S_0$ atomic transition (6892 Å for Sr, 6573 Å for Ca) and to promote the chemical reaction.

Two types of low-resolution spectra were recorded. Laser excitation spectra were obtained by scanning the probe laser through a spectral region where MSR ($M = \text{Ca}$ and Sr) absorb and detecting the total fluorescence through red-pass filters (Schott RG 695, RG 9, and RG 780) with a photomultiplier tube. Resolved fluorescence spectra were obtained by fixing the dye laser at the frequency of a CaSR or SrSR molecular transition and resolving the fluorescence with a small monochromator.

Results

A comparison of laser excitation spectra of CaSR and SrSR [$R = \text{H}$, CH_3 , C_2H_5 , C_3H_7 , $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$, and $\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$] is provided in Figures 1 and 2, respectively. The three observed electronic transitions are $\tilde{C}^2A'-\tilde{X}^2A'$, $\tilde{B}^2A''-\tilde{X}^2A'$, and $\tilde{A}^2A'-\tilde{X}^2A'$. The observed band centers for these transitions obtained from laser excitation and resolved fluorescence spectra are presented in Tables I and II.

The intensities of the features in these spectra are distorted. The red-pass filters used to eliminate the scattered laser radiation in recording the excitation spectra enhance some features over others. The relative intensities are also dependent on the output power of the dye laser.

In general for calcium thiolates, as the alkyl group becomes larger, the $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$ band centers shift to the red (Figure 1). The $\tilde{C}-\tilde{X}$ transition was not observed for calcium thiolates. For the strontium thiolates (Figure 2), the spectral shifts are similar. Note that the $\tilde{A}-\tilde{X}$ transition of both CaSH and SrSH shifts to the blue when the H is replaced by CH_3 . The $\tilde{C}-\tilde{X}$

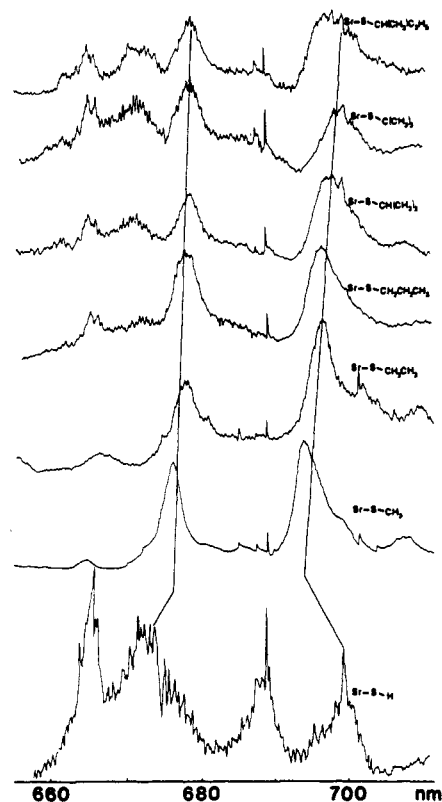


Figure 2. Laser excitation spectra of strontium thiolates. The corresponding transitions for the different thiolates are connected by a line. SrSH is also observed for the larger thiolates in the upper four panels. The sharp feature at 6892 Å is the $^3P_1-^1S_0$ atomic line of Sr, which excites the 1-0 vibronic band of the $\tilde{A}-\tilde{X}$ transition of SrSH.

transition is observed for SrSH, SrSCH_3 , and $\text{SrSCH}_2\text{CH}_3$.

Excitation spectra of larger thiolates show an almost identical spectral pattern. Since these electronic transitions involved metal-centered molecular orbitals, the nature of the alkyl group is expected to have a small effect on the transition energies. CaSH and SrSH were also observed in the spectra of larger thiolates and greatly mask the spectral features of the heavier thiolates. The $\tilde{C}-\tilde{X}$ transition of large Sr thiolates are probably obscured by the $\tilde{C}-\tilde{X}$ transition of SrSH. For calcium compounds, the $\tilde{B}-\tilde{X}$ transition is obscured by the $\tilde{A}-\tilde{X}$ transition of CaSH.

CaS and SrS ($A^1\Sigma^+-X^1\Sigma^+$ system) appeared as an impurity in many spectra.^{21,22} Changing the conditions in the oven also minimized the production of sulfides. The reaction of metal vapor with the thioethers (CH_3SCH_3 and $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$) and the disulfide, CH_3SSCH_3 , produced the strong features identical with those observed with the corresponding thiols, CH_3SH and $\text{CH}_3\text{CH}_2\text{SH}$. However, the larger thioethers and disulfides are not available with high purity and the vapor pressures are less than the thiols.

The observed electronic states for the alkaline earth thiolates can be explained with the aid of the energy diagram in Figure 3. The bonding and electronic structure in these molecules are described by an metal ion perturbed by the ligand. The thiolate spectra resemble the corresponding monohydroxides. The valence 4s, 3d, and 4p atomic orbitals of the Ca^+ ion give rise to the electronic states of CaOH. The OH⁻ ligand also mixes the parent atomic orbitals of the states so that, for CaOH, the $\tilde{B}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states are $p\sigma-d\sigma$ and $p\pi-d\pi$ mixtures. CaSH is a bent molecule and belongs to the C_2 point group. This symmetry lowering from $C_{\infty v}$ of CaOH lifts the degeneracy of the "in-plane" p/d orbitals and "out-of-plane" p/d orbitals. Therefore, the $^2\Pi$ state split into $^2A''$ (out-of-plane) and $^2A'$ (in-plane) states in CaSH. The $\tilde{A}^2\Pi$ and $\tilde{B}^2\Sigma^+$ states of CaOH become the \tilde{A}^2A' , \tilde{B}^2A'' , and \tilde{C}^2A' states of CaSH. The symmetry of the \tilde{A} , \tilde{B} , and \tilde{C} states is determined

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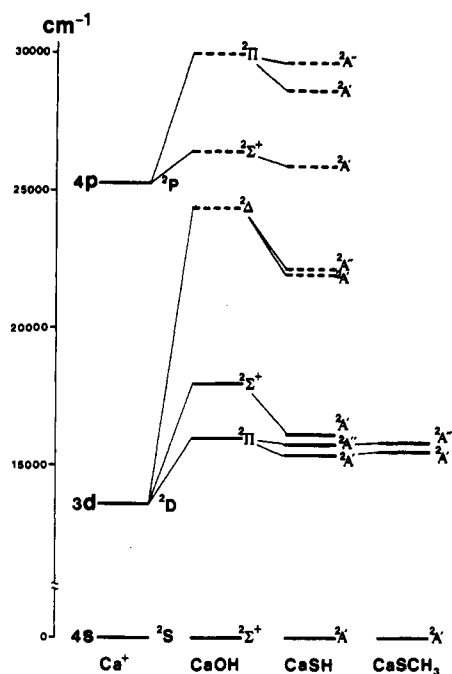


Figure 3. Correlation diagram showing the effects of various ligands perturbing the Ca^+ ion atomic orbitals. The solid lines represent the experimentally known electronic states, and the dashed lines represent the calculated electronic states from ref 19.

mainly by comparison with ab initio calculations of Ortiz.¹⁹ These calculations are consistent with some preliminary $\tilde{B}-\tilde{X}$ and $\tilde{A}-\tilde{X}$ rotational measurements of CaSH and SrSH.

In addition to the ab initio calculations¹⁹ and the observation of rotational structure consistent with an asymmetric top,¹⁸ the low-resolution spectra provide evidence for bent CaSH and SrSH structures. The excited-state spacing between the \tilde{A} and \tilde{B} states of CaSH (or SrSH, Tables I and II) corresponds either to the spin-orbit interval between the $\tilde{A}^2\Pi_{1/2}$ and $\tilde{A}^2\Pi_{3/2}$ spin components of an " $\tilde{A}^2\Pi$ " state of a linear molecule or to the interval between two electronic states \tilde{A}^2A' and \tilde{B}^2A'' for a bent molecule (Figure 3). In the case of a bent molecule the observed \tilde{A} and \tilde{B} states will correlate back to a single degenerate $\tilde{A}^2\Pi$ state (Figure 3). The $\tilde{A}-\tilde{B}$ intervals are 444 cm^{-1} for CaSH and 522 cm^{-1} for SrSH (Tables I and II) compared to the analogous $\tilde{A}-\tilde{B}$ intervals of 200 cm^{-1} for CaNH_2 and 450 cm^{-1} for SrNH_2 .²³ The observed $\tilde{A}-\tilde{B}$ intervals for CaSH and SrSH are inconsistent with all previously determined spin-orbit splittings in $\tilde{A}^2\Pi$ or \tilde{A}^2E states of related molecules, which range from 57 cm^{-1} (CaC_2H_2) to 76 cm^{-1} (CaN_3) for calcium derivatives and 255 cm^{-1} (SrC_2H_2) to 309 cm^{-1} (SrCH_3) for strontium derivatives. (A more complete tabulation of the various spin-orbit splittings is found in Table III of ref 24.) Thus, the electronic structure of CaSH and SrSH more closely resembles that of the CaNH_2 and SrNH_2 molecules than that of the linear CaOH and SrOH molecules.

In retrospect, a bent structure for CaSH and a linear structure for CaOH are reasonable because of the increased covalent character in the metal-sulfur bond. CaOH is linear because the bonding is almost completely ionic (Ca^+OH^-) so the lowest energy structure has the partially positive H of the OH^- group distant from the Ca^+ . In the isovalent CaSH case the SH group is less electronegative than the OH group, so the Ca-S bond has more covalent character. The increased covalent participation of the p orbitals on S in the metal-sulfur bond results in a bent CaSH molecule. An analogous effect occurs in the bent CuOH molecule^{25,26} where the Cu is now less electronegative than Ca so the

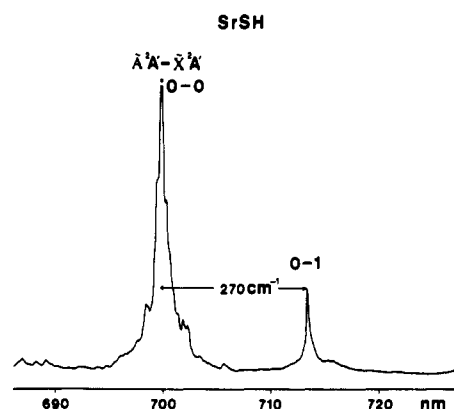


Figure 4. Resolved fluorescence spectrum of SrSH. The frequency of the probe dye laser was held fixed on the 0-0 band of the $\tilde{A}-\tilde{X}$ transition. The scattered laser light is marked by the asterisk. The feature at 7103 Å is emission to $v = 1$ of the Sr-S stretching vibrational level in the ground state.

TABLE III: Band Centers of CaSH (in cm^{-1}); Only the Ca-S Vibration Was Observed

band	$\tilde{A}^2A'-\tilde{X}^2A'$	$\tilde{B}^2A''-\tilde{X}^2A'$	$\tilde{C}^2A'-\tilde{X}^2A'$
0-2	14 730	15 177	15 456
0-1	15 040	15 492	15 770
0-0	15 366	15 810	16 082
1-0	15 684	16 129	16 402
2-0	15 973	16 453	16 730

TABLE IV: Band Centers of SrSH (in cm^{-1}); Only the Sr-S Vibration Was Observed

band	$\tilde{A}^2A'-\tilde{X}^2A'$	$\tilde{B}^2A''-\tilde{X}^2A'$	$\tilde{C}^2A'-\tilde{X}^2A'$
0-2	13 751		14 490
0-1	14 023	14 545	14 755
0-0	14 293	14 815	15 026
1-0	14 565		15 295
2-0			15 576

TABLE V: M-S Vibrational Frequencies of CaSH and SrSH (in cm^{-1})

molecule	\tilde{X}	\tilde{A}	\tilde{B}	\tilde{C}
SrSH	270	270		269
CaSH	326	318	320	312

metal-ligand electronegativity difference is also decreased, resulting in a bent geometry.

The Franck-Condon factors favor the vibronic bands that are associated with the metal atom, since the electronic transitions occur in the orbitals that are centered on the metal atom. Therefore, M-S stretching and M-S-H (or M-S-C) bending vibrations are expected in the spectra, but only a single mode is active in the spectra of the CaSH and SrSH molecules. The vibrational frequencies of $\sim 320 \text{ cm}^{-1}$ for CaSH and $\sim 270 \text{ cm}^{-1}$ for SrSH (Table V) are consistent with M-S stretching modes (Table VI). The bending modes are expected to have lower frequencies, and there is no evidence for any vibrational activity of the bending modes in the spectra. By the Franck-Condon principle this suggests that the bond angles are very similar in the ground and excited electronic states. If, for example, the molecule was linear in an excited " $\tilde{A}^2\Pi$ " state and bent in the ground \tilde{X}^2A' state, then a long progression in the bending mode would have been observed.

The resolved fluorescence spectrum of SrSH is provided in Figure 4. The probe dye laser is tuned to excite the 0-0 band of the $\tilde{A}^2A'-\tilde{X}^2A'$ transition. The sharp peak to the red (at 7130 Å) is assigned to the 0-1 band of the Sr-S stretch. The centers of the vibronic bands of CaSH and SrSH are given in Tables III and IV, respectively. For calcium and strontium thiolates, the

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TABLE VI: Comparison of the Ground-State Vibrational Frequencies of MSH, MOH, and MNH₂ (in cm⁻¹)

M	MOH ^a	MNH ₂ ^b	MSH ^c
Ca	606	524	326
Sr	528	459	270

^aReferences 6 and 15. ^bReference 23. ^cThis work.

laser-induced fluorescence was very relaxed and the vibrational bands were not clear. No vibrational information was seen in the resolved fluorescence spectrum. Excitation of $\tilde{B}-\tilde{X}$ or $\tilde{C}-\tilde{X}$ bands produced strong $\tilde{A}-\tilde{X}$ emission, probably through collisions and nonradiative decay processes. This type of strong relaxation to lowest excited state has been seen for metal monoalkylamides.²³ An attempt was made to record the laser excitation spectra by using the monochromator as a band-pass filter to detect the vibronic bands. These experiments gave identical spectra to those which were recorded with the red-pass filters.

The M-S stretching frequencies for SrSH and CaSH are given in Table V. The frequencies in all four electronic states are almost the same. Table VI compares the ground-state vibrational frequencies of M-SH with M-OH and M-NH₂. The M-S stretching frequencies are less than the corresponding M-O and M-N (even when the heavier S mass is taken into account), indicating that the force constants are smaller in metal hydrosulfides. This suggests that dissociation energies are smaller than the corresponding M-OR and M-NHR dissociation energies.

Conclusion

The calcium and strontium thiolates were produced in the gas phase by the reaction of the metal vapor with the appropriate thiol. The laser excitation spectra of three electronic transitions $\tilde{C}^2A'-\tilde{X}^2A'$, $\tilde{B}^2A''-\tilde{X}^2A'$, and $\tilde{A}^2A'-\tilde{X}^2A'$ were recorded. By implication, the M-S-C angle in the thiolate derivatives is also not 180°. The observation of a bent CaSH is in contrast to a linear CaOH and suggests considerable covalent character in the Ca-SH bond.

The experimental results are in excellent agreement with the theoretical calculations of Ortiz.¹⁹ These calculations were very helpful in our interpretation of the electronic structure of the alkaline earth thiolates. The ab initio electron propagator calculations seem to have captured the simple one-electron character of the observed electronic transitions.

Acknowledgment. This research was supported by the National Science Foundation (Grants CHE-8608630 and CHE-8913785).

Registry No. CaSH, 104839-21-6; CaSCH₃, 131794-11-1; CaSC-H₂CH₃, 131794-12-2; CaSCH₂CH₂CH₃, 131794-13-3; CaSCH(CH₃)₂, 131794-14-4; CaSC(CH₃)₃, 131794-15-5; CaSCH(CH₃)C₂H₅, 131794-16-6; H₂S, 7783-06-4; CH₃SH, 74-93-1; CH₃CH₂SH, 75-08-1; CH₃C-H₂CH₂SH, 107-03-9; (CH₃)₂CHSH, 75-33-2; (CH₃)₃CSH, 75-66-1; CH₃CH₂CH(CH₃)SH, 513-53-1; SrSH, 104839-22-7; SrSCH₃, 131794-17-7; SrSCH₂CH₃, 131794-18-8; SrSCH₂CH₂CH₃, 131794-19-9; SrSCH(CH₃)₂, 131794-20-2; SrSC(CH₃)₂, 131794-21-3; SrSCH(C-H₃)C₂H₅, 131794-22-4; Ca, 7440-70-2; Sr, 7440-24-6.

Comparative Study of Stimulated Proton-Transfer Luminescence of Three Chromones[†]

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The contrasting behavior of three related chromones with respect to amplified spontaneous emission (ASE) and lasing action as *intramolecular proton-transfer laser* systems at room temperature is investigated. The intramolecular proton-transfer laser is considered a chemical laser in which the excited tautomer species is produced by a chemical reaction after photon-pumping, activating a four-level laser system. The three chromones studied are 2-methyl-3-hydroxychromone, 2-phenyl-3-hydroxychromone (3-hydroxyflavone), and the natural product fisetin (3,3',4',7-tetrahydroxyflavone), each of which exhibits good proton-transfer fluorescences in the 500-nm region, with respective quantum yields of 0.29 (MCH), 0.36 (MCH), and 0.16 (dioxane). Low-temperature spectroscopic study and picosecond transient absorption spectroscopy reveals that fluorescence quenching from molecular aggregation and transient parasitic S_n' ← S₁' absorption of the tautomer both contribute to nonobservability of ASE and lasing action in the 2-methyl-3-hydroxychromone, in contrast to excellent ASE/lasing characteristics of the 3-hydroxyflavone and fisetin under comparable conditions.

Proton-Transfer Fluorescence and Stimulated Emission in Chromones

The spectroscopic and laser excitation dynamics studies of *o*-hydroxychromones have brought new understanding of the intramolecular proton-transfer process in internally hydrogen-bonded molecules. The picosecond rise times for tautomer formation upon electronic excitation have permitted a wide range of transient absorption studies, revealing the intricate spectroscopy of these systems. New avenues for photochemical product formation have been revealed, as well as the possibility of generating high population inversions for the tautomer lowest excited singlet state, leading to an efficient proton-transfer laser.

The intramolecular proton-transfer laser may be considered as an extension of the class of *chemical lasers* pioneered by George

Pimentel. In the prototype chemical laser a *chemical* reaction leads to an excited species that then exhibits lasing action. In this intramolecular proton transfer case, a new chemical species is produced in an excited state and subsequently may exhibit lasing action—although in this case the initial step is a *photochemical* reaction. A suitable internally H-bonded excited molecule may undergo an intramolecular proton transfer on a picosecond time scale, and a new chemical species (the tautomer) with complete electronic rearrangement is formed (in its lowest excited state). The population inversion is very high, as the tautomer ground state is empty, and the rapid reverse proton transfer to the normal ground state serves to maintain the exceptional population inversion. The consequence of this four-level laser mechanism is an extraordinarily high gain factor, as well as a very large wavelength shift away from normal molecule spectral interference.

The substituted chromones include a very wide variety of flavonols occurring as natural plant pigments. The comparative spectroscopic and laser studies of these have exposed some unexpected paradoxes. In this paper we compare the spectroscopic and stimulated emission properties of 2-methyl-3-hydroxy-

[†]This paper is dedicated to the memory of George Pimentel, our most esteemed and admired great colleague, a pioneer in matrix spectroscopy and chemical lasers.

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