

FIG. 2. Observed probe signal intensity as a function of (pump-probe) delay time for the pyrazine origin. The pump wave length is 3238.5 Å and the probe is two photons at 4026 Å (see the text). The solid line through the data is the computed best fit which yields a decay time constant of 118 ± 16 ps. Note that the ratio of the fast/slow decay components is determined by the efficiency of ionization by the probe pulse and comparison with fluorescence ratio requires details of the kinetics (Ref. 14). Pyrazine was seeded in pure He at a packing pressure of 30 psi.

UV pulse over a range of 532 ps. The fast exponential at the pyrazine origin ($30\,876\text{ cm}^{-1}$) is 118 ± 16 ps. The slow exponential, which is known to be on the microsecond time scale, is flat over our time period. The decay curve with computed best fit is shown in Fig. 2.

From the data presented here it is evident that the fast component does not follow the response of our short pulse. Instead, we observe a decay component of 118 ps after the pulse is turned off. This indicates that the decay is not Rayleigh-type scattering and it is indeed *molecular* in nature. Furthermore, the result also removes the doubt⁹ that a Rayleigh wing can be responsible for observations made by pulses (or detection responses) with duration comparable to the dephasing time, i.e., the 118 ps. A reexamination of the

nature of ME's¹ is now needed.¹³ A full account of our picosecond work will be published later when we complete work on deutropyrazine and other azines.

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^{b)} Contribution No. 7108. This work was supported by grant No. DMR-8105034 from the National Science Foundation.

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Laser spectroscopy of organometallic free radicals

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(Received 10 September 1984; accepted 9 November 1984)

We have observed more than a dozen new organometallic free radicals. Calcium and strontium have been found to react in the gas phase with a wide variety of organic molecules including aldehydes, ketones, alcohols, and carboxylic acids. The reaction products are free radical metal salts with electronic states closely related to the alkaline earth monohalides. The reactions occur with ground state reagents, however, an enhancement of more than three orders of magnitude in the concentration of products was observed using laser excitation of the metal atoms.

The first new molecule was observed when acetone was inadvertently introduced into a Broida oven¹ containing Sr vapor. In such a system, metal atoms are evaporated from a resistively heated crucible, entrained in an argon carrier gas and then allowed to react with a suitable oxidant.¹ Figure 1 shows a laser excitation spectrum of the Sr plus acetone reaction obtained by scanning a broad band (1 cm^{-1}) cw dye laser and detecting the total fluorescence. The *Q* heads of SrOH $A^2\Pi_{1/2}-X^2\Sigma^+$ appear²⁻³ near the Sr atomic line ($^3P_1-^1S_0$) and 270 cm^{-1} to the blue are the $A^2\Pi_{3/2}-X^2\Sigma^+$ *Q* heads.

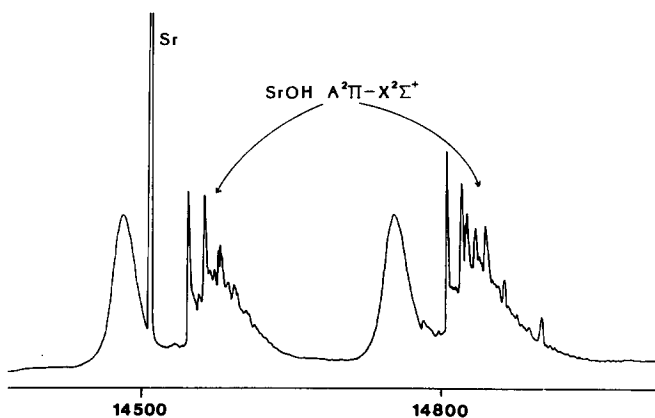


FIG. 1. Laser excitation spectrum of the Sr plus acetone reaction products. The two broad peaks are due primarily to the strontium isopropoxide radical.

The broad features at 6777 and 6903 Å located to the red of the sharp SrOH Q heads are also separated by 270 cm^{-1} and are due to a new molecule. A similar spectrum is observed with calcium and acetone but the peaks are at 6292 and 6319 Å separated by 68 cm^{-1} very close to the CaOH spin-orbit splitting of 67 cm^{-1} .⁴⁻⁶ The similarity of the new molecules with the corresponding hydroxides implies that the *local* metal symmetry is linear with the metal atom bonded to oxygen.

When the dye laser was fixed on one of the new features, fluorescence spectra were obtained by scanning a 0.64 m monochromator. The laser induced fluorescence spectra of the products of the Ca and Sr reactions with ethanol and isopropanol were also observed and found to be almost identical with the corresponding acetaldehyde and acetone spectra. The major products of the Ca(Sr) reaction with ethanol, acetaldehyde, isopropanol and acetone were thus Ca(Sr) ethoxide and Ca(Sr) isopropoxide. The calcium (Sr) metal had reduced the acetone and acetaldehyde so mainly alcohol derivatives were observed. The Ca-O (Sr-O) stretching fre-

quencies in the ground states were found to be 387 cm^{-1} for Ca-O-Et (335 cm^{-1} , Sr-O-Et) and 319 cm^{-1} for Ca-O-iPr (276 cm^{-1} , Sr-O-iPr). The reactions with acetone and acetaldehyde produced spectra with some additional features (not found in the alcohol reactions) which we speculatively attribute to enol salts, e. g., Ca-O-C(CH₂)CH₃.

The bonding in these molecules is largely ionic and the electronic transitions occur between M^+ centered atomic-like orbitals perturbed by an ^-O-R ligand. Thus, the exact nature of R has a rather small effect of the electronic structure.

Inspired by these results we investigated the reactions of calcium and strontium with formic and acetic acid. Figure 2 is a laser excitation spectrum of the Sr plus formic acid reaction. The reaction produced SrH and SrOH as well as a new molecule with peaks at 6785 and 6710 Å separated, not by 270 cm^{-1} but by 165 cm^{-1} . We assign the carrier of this spectrum to the strontium monoformate radical with C_{2v} symmetry. The two main peaks are the 2B_1 and 2B_2 electronic states that correlate⁷ with the $A\ ^2\Pi$ state of SrF. A monochromator scan with the laser fixed at 6785 Å establishes the symmetric metal-oxygen stretch to be 280 cm^{-1} in the ground (2A_1) state. A new electronic transition was also found 1000 cm^{-1} below the 6785 Å peak. This new electronic state probably has 2A_1 symmetry and correlates with one component of the expected $^2\Delta$ states of strontium monohalides.⁸ The $^2\Delta-^2\Sigma$ transition has become allowed ($^2A_1-^2A_1$) in a C_{2v} molecule.

We are currently extending this work to barium containing compounds as well as to metal plus alcohol reactions and metal plus amine reactions. A rotational analysis of calcium monomethoxide is underway.⁹ More detailed accounts of our work will be published in the near future. The new molecules that we have found are important model compounds for more complicated transition metal organometallics and for chemisorbed surface species.¹⁰ They may also be

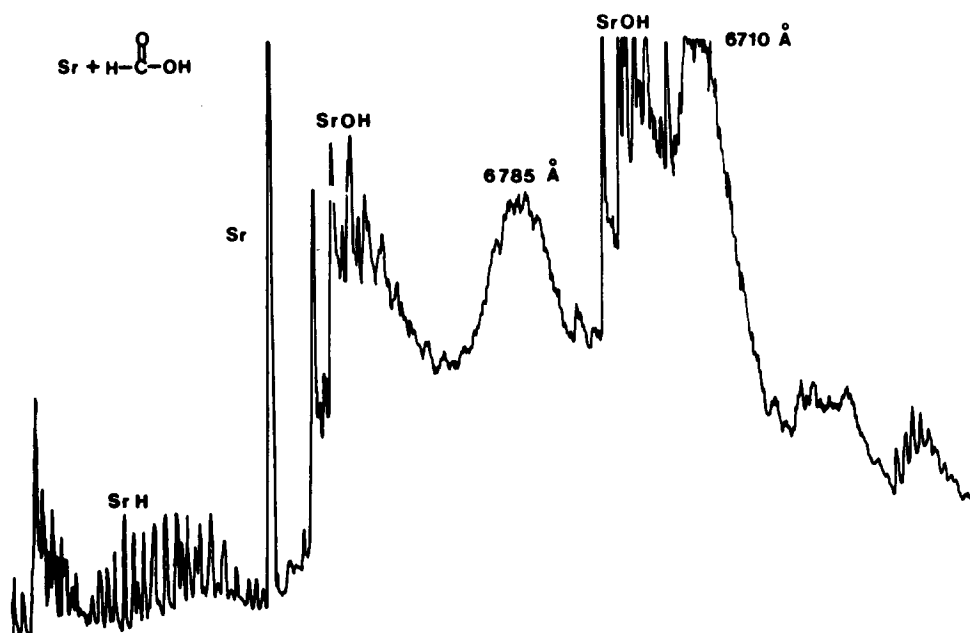


FIG. 2. Laser excitation spectrum of the Sr plus formic acid reaction products. The strontium monoformate radical is responsible for the 6785 and 6710 Å peaks.

important in interstellar chemistry occurring on grain surfaces.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. This research was also supported by grants from the National Science Foundation (CHE-8306504) and the Research Corporation.

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Difference frequency laser spectroscopy of the ν_1 band of HOCO^+

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(Received 1 October 1984; accepted 7 November 1984)

In 1981, Thaddeus, Guelin, and Linke¹ attributed three harmonically related unidentified millimeter-wave lines observed in SgrB2 to either HOCO^+ or HOCN . Later DeFrees *et al.*² suggested that HOCO^+ was the more likely candidate, based on a comparison of the *ab initio* calculated rotational constants with the "observed". Several attempts³ have been made in various laboratories to detect the microwave lines of HOCO^+ for conclusive confirmation of this tentative assignment. Quite recently, Bogey, Demuynck, and Destombes⁴ finally succeeded in detecting submillimeter-wave absorption lines of HOCO^+ around 370 GHz. In this Communication, we report the first observation of the infrared spectrum of this ion, thus providing an independent confirmation of the identification of interstellar HOCO^+ .

The experimental technique used in the present work is similar to that in our previous experiments.⁵ One modification made here was that a hollow cathode discharge cell replaced the previous conventional glow discharge cell. The hollow cathode cell is of similar design to that employed by Foster *et al.*⁶ and Foster and McKellar.⁷ Some preliminary tests⁸ done by monitoring the lines of H_3^+ , H_2D^+ , and HCO^+ indicated that the signal intensity was enhanced at least by an order of magnitude compared with that obtained using our previous glow discharge cell.

The HOCO^+ ions were generated in a modulated discharge through a flowing gas mixture of CO_2 (20 mTorr) and H_2 (250 mTorr). The discharge was cooled by allowing methanol at about -50°C to flow through copper tubing wound around the cathode. The discharge modulation frequency was 5 kHz, and the optimum peak current was about 800 mA. The application of an axial magnetic field of 150 G to the cathode glow resulted in almost total loss of the ion signals⁸ similar to the effect reported by Saito *et al.*⁹ This phenomenon has been observed also on the known ions such as H_3^+ , H_2D^+ , and HCO^+ .⁸

The HOCO^+ is a bent molecule with an almost linear O-C-O structure.¹⁰⁻¹² Both the *a*-type and *b*-type transitions were observed. At first it was noticed that the spectral

pattern repeated itself with approximately 0.7 cm^{-1} interval, and the lines were readily assigned to the *a*-type *P*- and *R*-branch transitions. Figure 1 is an example of the signals which are assigned to the $^P Q_1(J)$ transitions with partial overlaps by *P*- or *R*-branch lines. At the present stage, nearly 300 lines have been observed. The transition wave numbers were measured with N_2O lines as reference,¹³ and the accuracy of our measurement is estimated to be better than 0.001 cm^{-1} . The difference between the frequencies for $^9R_0(15)$ and $^9P_0(17)$ transitions was found to be 705 454 MHz which agreed within our measurement accuracy with the sum of the transition frequencies of the $J=17-16, K=0$ and the $J=16-15, K=0$ lines observed by Bogey *et al.*⁴ A similar check was done on the $K=2$ lines.

A preliminary least-squares fit was made with a standard asymmetric-top Hamiltonian in the *A*-reduced representation,¹⁴ including 176 lines of the *a*-type *P*- and *R*-branch lines of $K=0, 1$, and 2, and the *b*-type *Q*-branch lines of $K=0-1$ and $K=1-0$. The rotational constants, B_0

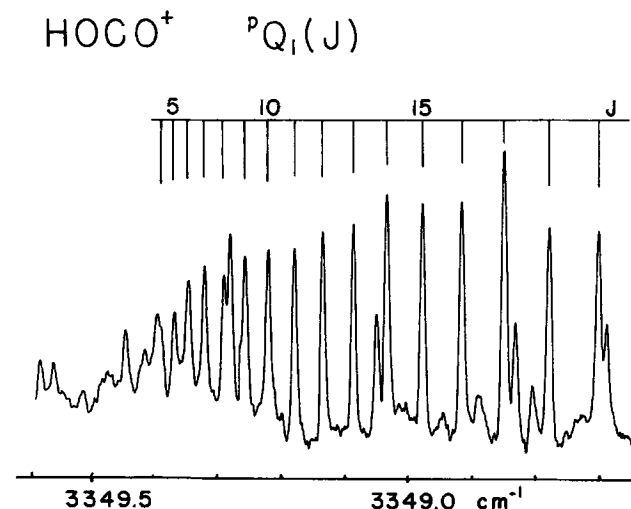


FIG. 1. The $^P Q_1(J)$ transitions of the ν_1 band of HOCO^+ recorded with a 0.4 s time constant.