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COMMUNICATIONS

Metal cluster oxidation: Chemiluminescence from the reaction of sodium polymers (Na_n , $n \geq 3$) with halogen atoms ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)

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The structure and bonding of small metal clusters represents a young topic which has become the focus of both experiment and theory.¹ The emphasis now placed on the study of the basic properties of these clusters stems, in part, from their possible importance to the understanding of the fundamental mechanisms of catalysts and numerous chemical conversions. Ligand-free metallic clusters have been produced in the gas phase through "free jet" supersonic expansion of the pure element^{1(a),1(b),2} and through select cluster deposition³ or diffusion controlled clustering^{1(a),1(b)} in rare gas matrices. Emphasis has been primarily on spectroscopic characterization of the produced cluster with little focus on the binding energies of these species or "cluster oxidation." In studying gas phase metal cluster oxidation, we are afforded the opportunity to characterize the intermediate region bordered on the one side by the gas phase oxidation of metallic atoms and dimers and on the other by the surface oxidation of the bulk metallic phase. It is thought⁴ that these studies will provide information which may be useful for the assessment of short and long range factors affecting surface oxidation.

This report outlines the first study of phenomena associated with gas phase polymeric sodium cluster oxidation. Initial efforts focus on oxidation with the halogen atoms chlorine, bromine, and iodine. These systems were chosen (1) because of their analogy to the previously studied⁵ alkali dimer-halogen atom reactions and (2) because of the higher electronic transition moments generally characteristic of compounds of the alkali metals.⁶

The apparatus used in these studies will be described in more detail in a future report.⁷ Briefly, the system consists of oven and reaction chambers connected by a variable sized channel 20 mm in length which, in the present experiments is 6 mm in diameter. Sodium is expanded from a stainless steel double oven used for the supersonic expansion of alkali metals.^{1(b)} The oven

was run at stagnation pressures between 20 and 120 Torr and the expansion nozzle diameter was typically 0.25 mm. The separation between nozzle orifice and fluorescence zone is approximately 17 cm and the molecular beam density in the fluorescence zone ranges to a maximum of $\approx 10^{13}$ particles/cm³. The halogen atom gun is operated at temperatures in excess of 1500 K whence halogen molecules passing through the gun channel should be 95+% converted to halogen atoms. The system is operated in a beam-gas configuration. Pressures in the reaction chamber never exceeded 5×10^{-5} Torr. In order to maintain these conditions and insure smooth oven operation, liquid nitrogen cooling was used throughout the oven and reaction chambers.⁷

Figure 1 depicts the chemiluminescent emission which characterizes the exemplary sodium-chlorine system under two distinct experimental conditions. If the halogen atom gun is operative and the sodium beam is generated supersonically [Fig. 1(a)], we observe a molecular spectrum characterized in large part by strong emission corresponding to the $\text{Na}_2^* B^1\Pi_u - X^1\Sigma_g^+$ band system⁸ and moderate emission associated with the $\text{Na}_2 A^1\Sigma_u^+ - X^1\Sigma_g^+$ and $C^1\Pi_u - X^1\Sigma_g^+$ band systems. In addition, weak emission is tentatively attributed to the $\text{Na}_2 D$ and E states.^{8,10} Although not indicated in Fig. 1(a), the molecular emission characterizing the supersonic sodium-chlorine atom reaction is dominated by intense emission corresponding to both the Na D -line and $4^2P - 3^2S$ sodium atom transitions.¹¹ There are also other emission features not readily associated with Na_2 or Na which are currently the subject of continued investigation in our laboratory. Most notable among these is the 3900 Å feature in close proximity to a region of the $\text{Na}_2 C-X$ emission system. Based upon a comparison of the spectra characterizing both the chlorine and bromine atom reactions, this feature is molecular in origin and associated with a homonuclear sodium compound.

Over the range of oven conditions considered, the Na_2

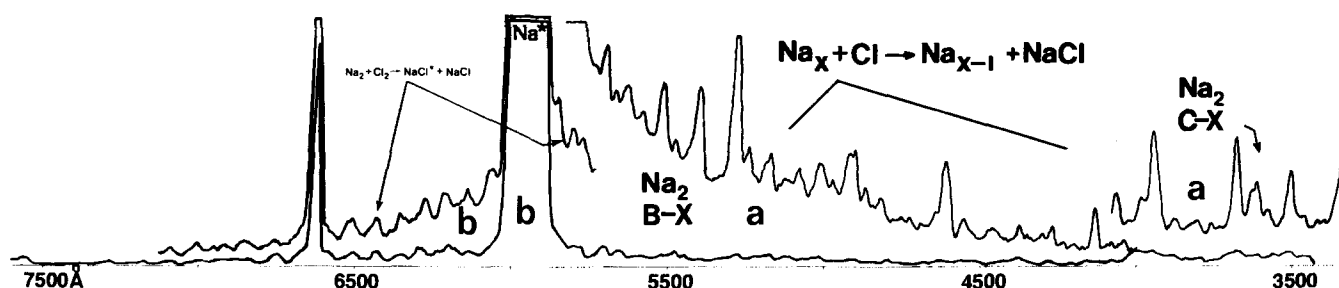
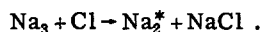


FIG. 1. (a) Chemiluminescent spectrum (3400–5800 Å) associated with the processes $\text{Na}_x + \text{Cl} \rightarrow \text{Na}_{x-1} + \text{NaCl}$, where the dominant molecular spectrum corresponds to Na_2^* emission resulting primarily from the reaction of sodium trimer. The major features in the B–X and C–X regions correspond to the overlap of several (v', v'') emission features (e.g., for the 5278 Å feature the intensity is derived primarily from $\Delta v = v' - v'' = -9, -8$, transitions...). Below 4100 Å, the scale for the C–X region is multiplied by 4. At the long wavelength limit, the emission rises sharply as the Na D-line is approached. The Na atomic emission features ($\text{Na}; 3^2P-3^2S, 4^2P-3^2S$), not depicted, are $\sim 10^2$ times the intensity of the molecular emission features. (b) Chemiluminescent spectra for NaCl^* and Na^* . The NaCl^* emission is tentatively attributed to the reaction $\text{Na}_2 + \text{Cl}_2 \rightarrow \text{NaCl}^* + \text{NaCl}$. The observed strong Na^* fluorescence is consistent with the process $\text{NaCl}^* + \text{Na} \rightarrow \text{Na}^* + \text{NaCl}^*$. The feature at 6600 Å corresponds to second order emission associated with the Na 4^2P-3^2S transition. In contrast the $\text{Na}_2 + \text{Cl}$ reaction leads only to atomic emission corresponding to the Na D-line and 4^2P-3^2S transition. See the text for discussion.

component of the supersonic sodium beam is expected to range from approximately 0.3%–2%^{1(a),1(b),3} corresponding to a concentration of 10^9 to $10^{11}/\text{cm}^3$. The intensity of the Na_2 emission depicted in Fig. 1(a) appears to parallel closely the expected Na_3 concentration in the sodium beam and, in addition, appears to vary linearly with the chlorine atom concentration. Hence, we associate the Na_2 chemiluminescence primarily with the reaction¹²



The spectra observed for the sodium–bromine system are similar to those observed for sodium–chlorine; however, there clearly is a decrease in excitation due to decreasing reaction exoergicity and the emission observed at shorter wavelengths is correspondingly diminished. A much more pronounced intensity dropoff characterizes the sodium–iodine system.

Figure 1 is drawn to emphasize the significant changes which are associated with the presence of sodium clusters and chlorine atoms. The $\text{Na}_n\text{–Cl}$ emission spectrum should be compared with that obtained when the chlorine gun is not operative, i.e., when only molecular chlorine interacts with either the products of a supersonic or effusive sodium beam. An example of this spectrum is indicated in Fig. 1(b) labeled as that which is to be associated with the $\text{Na}_2 + \text{Cl}_2$ metathesis. This spectrum, which consists of a very strong Na D-line emission, moderate Na 4^2P-3^2S emission, and weak features associated with an NaCl band system, can be viewed as a “background” spectrum for the emission associated with the supersonically expanded sodium–chlorine atom reaction. The two spectra depicted in Fig. 1 differ only in that when the chlorine atom source is operative, Na_2^* emission is observed over the wavelength range 3200–5500 Å. This emission is conspicuously absent otherwise. We find, in agreement with other workers,¹³ that this background emission is virtually identical to that associated with the products of an effusive sodium (monomer + dimer) – chlorine molecule interaction. Therefore, based on reaction exoer-

gicities,¹⁴ we tentatively associate the NaCl emission in the region of the Na D-line with the four center process $\text{Na}_2 + \text{Cl}_2 \rightarrow \text{NaCl}^* + \text{NaCl}$ although a more complicated metathesis might be operative. In further experiments,¹⁵ we have assessed the emission spectra which are associated with the reaction of chlorine atoms and sodium dimers. In agreement with the results of Struve *et al.*⁵ only sodium atomic emission corresponding to the Na D-line and Na 4^2P-3^2S transitions is observed.

We have summarized the results of initial efforts in our continuing study of sodium cluster oxidation.¹⁶ A more detailed analysis of the features associated with Reaction (1) indicates the population of minimum of 18 vibrational quantum levels in the $C^1\Pi_u$ state of Na_2 . The association of the Na_2^* emission in Fig. 1 with sodium trimer oxidation provides a route for the estimation of the sodium trimer bond energy. This estimate will soon be obtained through use of our combined studies of chlorine, bromine, and iodine oxidation.

^{1(a)} A. Herrmann, M. Hofmann, S. Leutwyler, E. Schümacher, and L. Wöste, *Chem. Phys. Lett.* **62**, 216 (1979); (b) J. L. Gole, G. J. Green, S. A. Pace, and D. R. Preuss, *J. Chem. Phys.* **76**, 2247 (1982); (c) M. A. Duncan, R. E. Dietz, and R. E. Smalley, *J. Am. Chem. Soc.* **103**, 5245 (1981); (d) V. E. Bondybey and J. H. English, *J. Chem. Phys.* **74**, 6878 (1981) and references discussed in these articles.

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- ¹²The assignment of observed Na₂ fluorescence to Reaction (1) is also consistent with the apparent relatively high bond energies of the higher sodium clusters, Na_n, *n*=4,5 [J. Flad, H. Stoll, and H. Preuss, *J. Chem. Phys.* **71**, 3042 (1979); S. C. Richtsmeier, D. A. Dixon, and J. L. Gole, *J. Phys. Chem.* (in press)] and their abundance relative to sodium trimer. It is unlikely that a reactive encounter between atomic chlorine and sodium tetramer or pentamer will produce a sodium dimer excited state.
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- ¹⁵It has also been determined that the Na₂^{*} emission spectrum in Fig. 1(a) cannot be associated with the interaction of effusively or supersonically expanded sodium and CCl₄ (*x*=1-4) compounds formed via reaction of chlorine atoms or molecules with the surface of the hot carbon gun.
- ¹⁶Current research efforts include deflection studies to characterize molecular ions formed in reaction and the extension of the present single collision studies in a controlled manner to the multiple collision pressure range [J. L. Gole and S. A. Pace, *J. Chem. Phys.* **73**, 836 (1980); A. W. Hanner and J. L. Gole, *ibid.* **73**, 5025 (1980); G. J. Green and J. L. Gole, *Chem. Phys.* **46**, 67 (1980)].

Highly excited HCN: The inapplicability of classical dynamics^{a)}

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The classical stochastic transition in molecular systems is of current interest.^{1,2} The stochastic transition occurs when the phase space trajectory of a coupled system with *N* degrees of freedom no longer resides on an *N*-dimensional subspace ("invariant toroid") of 2*N* dimensional phase space. With this jump to higher dimensionality, the motion of the system becomes "stochastic." Trajectories which remain on an invariant toroid are called "quasiperiodic." The stochastic transition occurs at an energy where the measure of stochastic trajectories is nonzero. Although the relation between classical stochastic trajectories and quantum stochasticity is not understood, it is generally believed that there is a close connection.^{2,3} One reason for this is that semiclassical methods of quantization break down if the trajectories are stochastic. It is believed that above the stochastic transition on the wave functions are strongly mixed and cannot be well described by a set of "zero-order" functions. Also, the eigenvalues and wave functions depend critically on small changes in parameters in the problem (e.g., rotational angular momentum, atomic masses, etc.), and rapid intramolecular *v-v* relaxation takes place.

Very few of the classical trajectory calculations to date have been done on realistic molecular potential surfaces (see, however, Ref. 4). For our calculation, we chose a potential⁵ for HCN that has been parameterized to give: (1) the structure and force constants for HCN; (2) the structure and force constants for HNC;

(3) the calculated barrier to rearrangement; (4) the correct dissociation energies for all possible diatomic fragments; and (5) a modified Rydberg potential fitted to spectroscopic data for the resulting diatomic fragments. The calculated anharmonic potential constants for HCN and HNC from this surface agree very well with the results for fits to spectroscopic observations. Also, variational calculations on this surface give very good agreement for the fundamental frequencies. This is the only potential that we are aware of that is reasonably accurate over the entire configuration space of HCN.

The classical trajectories were started by placing the atoms at rest, and displacing the C-N distance and bond angle to the limit of their zero-point motion. The initial C-H distance was varied to deposit different amounts of energy in the C-H stretching motion. Then Hamilton's equations were integrated with both Given's and Gear algorithms, with the same results. Following a trajectory for 8.33 ps took about 18 min of cpu time of a VAX-11 computer. The calculations were so time consuming because (1) the potential contains four different exponential terms, and (2) the repulsive wall is very steep, so that small integration steps are required near the wall.

Since a trajectory cannot be integrated for infinite time, the dimensionality of the trajectory cannot be directly checked. The most common procedure for