corresponding to CO(v=1). From the signal-to-noise ratio of our spectra, we place an upper limit of 2% on the amount of CO(v=1) produced by the dissociation. It thus appears that the CO product of OCS dissociation at 222 nm is formed in very excited rotational levels but almost entirely in $V = 0$.

Dissociation of OCS Clusters. The most striking result of our study is the observation of state-resolved photodissociation of OCS clusters. Figure 3 shows the region of the CO (2,0) band head near 67 625 cm^{-1}, which is interspersed in the high rotational lines of the (3,0) band. The (2,0) band head is barely visible at $\simeq$67 637 cm^{-1} in Figure 3a, for which the partial pressure of OCS behind the nozzle is 40 torr, but it is clearly observed in Figure 3b, for which the partial pressure is 400 torr. The CO rotational distribution from the band head region is roughly Boltzmann with a temperature of 50 K.

Several observations indicate that this rotationally cold CO results from dissociation of OCS clusters: (1) Detailed experiments[25] show that the integrated intensity of the (2,0) band head increases as the square of the OCS partial pressure behind the nozzle, while the integrated intensity of the high rotational lines increases somewhat less than linearly. (2) The presence of clusters in our nozzle source has been confirmed in separate experiments using a quadrupole mass spectrometer. Large clusters, up to $(OCS)_8$, were observed with 400 torr of OCS behind the nozzle, while only monomers and some dimers were observed with an OCS partial pressure of 40 torr. (3) Appearance times for lines in both the band head region and the high-J region were obtained by delaying the pulsed probe laser relative to the dissociation laser. In both cases the CO intensity appeared in less than 50 ns, the time required for our photomultiplier to recover from scattered laser light, and no subsequent rise was observed. Rotational relaxation of CO($J \simeq 55$) to CO($J<5$) on this time scale can be ruled out, since the cross section for such a process would have to be in excess of 150 Å^2. It thus appears that the rotationally cold CO results from dissociation of OCS clusters.

Dissociation of $(OCS)_x$ also resulted in chemical reaction between weakly bound components of the van der Waals cluster. Both $S_2(^3\Sigma_g^-)$ and $S_2(^1\Delta_g)$ were identified as products of the dissociation by laser-induced fluorescence experiments similar to those reported by van Veen et al.[27] Like the cold CO, the S_2 signals appeared in less than 50 ns following the photolysis laser pulse and did not increase with time. Production of S_2 by reaction $S(^1D) + OCS \rightarrow S_2 + CO$ can be ruled out since such rapid formation would require a cross section greater than 600 Å^2 whereas the cross section for this reaction is at most 15 Å^2.[27,28] Thus, the S_2, as well as the cold CO, must be caused by dissociation of a cluster.

The most plausible explanation of these observations is that absorption of the 222-nm photon by the cluster results in dissociation of one of the OCS members, the major products being $S(^1D)$ and CO. Both of these species will be created initially in close proximity to the remainder of the cluster. The $S(^1D)$ might then react rapidly with a second OCS in the cluster to yield S_2 + CO, accounting for the observed S_2. The low rotational levels of CO detected as a result of cluster dissociation might be created either from relaxation of the original CO as it escapes the cluster or from the reaction of the $S(^1D)$ with the second OCS member. In any case, it is clear that the dynamics for dissociation of the cluster is considerably different than that for dissociation of the monomer and that chemical reaction has occurred between weakly bound components of the van der Waals cluster.

Conclusions

In summary, we have found that dissociation of the OCS monomer at 222 nm produces both $S(^3P)$ and $S(^1D)$, that the branching ratio for the former of these two channels is 0.15 ± 0.05, and that the CO formed in the dissociation is rotationally excited, peaking at $J = 55$, but vibrationally cold. Dissociation of OCS clusters had also been observed and produces CO which is rotationally cold ($T_{rot} \simeq 50$ K) and S_2 which is formed by chemical reaction between the weakly bound components of the van der Waals cluster.

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New Chlorite Oscillators: Chlorite–Bromide and Chlorite–Thiocyanate in a CSTR[1]

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The reactions between ClO_2^- and Br^- and between ClO_2^- and SCN^- show sustained oscillations in a stirred tank reactor. The former system possesses a broad region of bistability and is quite sensitive to the rate of stirring. The chlorite–thiocyanate reaction, in contrast, does not exhibit bistability. Oscillations without bistability have also been found in the reactions of ClO_2^- with two thiourea derivatives.

Introduction

Chlorite-based systems have played a key role in the study of chemical oscillation. The first systematically designed chemical oscillator[3] was a chlorite reaction, and chlorite oscillators have been found to exhibit a wide range of related phenomena from spatial pattern formation[4] to chemical chaos.[5]

The chlorite oscillators discovered to date[6] all involve either iodine-, bromine-, or sulfur-containing species. Among the largest group, the chlorite–iodine oscillators, the ClO_2^-–I^- system is

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particularly significant. It is the "minimal" member of this family, from which the others may be derived,[1] and it is the first of these reactions for which a mechanism has been developed. Thus far all chlorite–bromine oscillators[7] have contained BrO_3^- and have been treated mechanistically as modified bromate oscillators.[8] Only two chlorite–sulfur oscillators, ClO_2^-–$S_2O_3^{2-}$ (ref 9) and ClO_2^-–$SC(NH_2)_2$,[10] are known. Both appear to be extremely complex stoichiometrically and in terms of the variety of dynamical phenomena they exhibit. Nothing is known about the mechanism of either.

By analogy with the minimal ClO_2^-–I^- system one might suspect that other halide or pseudohalide ions might be likely candidates for participation in "simple", two-component chlorite oscillators. We report here two successful applications of that notion: the reactions of bromide and of thiocyanate ions with chlorite in a stirred tank reactor (CSTR) both give rise to oscillatory behavior. The former reaction may serve as a prototype for, and is certainly a component of, the more complex chlorite–bromate–substrate oscillators. The ClO_2^-–SCN^- system may prove more amenable to mechanistic analysis than the other known chlorite–sulfur oscillators. We also report the discovery of oscillatory behavior in the reactions of ClO_2^- with two thiourea derivatives.

Experimental Section

The CSTR experiments were performed in a plexiglass reactor of volume 14 mL thermostatted at 25.0 ± 0.1 °C. A platinum redox electrode (and in the ClO_2^-–Br^- system a Br^--selective (Orion) electrode) was employed in conjunction with a $Hg|Hg_2SO_4||K_2SO_4$ reference electrode. Stirring rates were measured with a stroboscopic light source. The three input streams consisted of the chlorite solution (see below), the bromide or thiocyanate solution, and, depending upon the pH desired, either a sulfuric acid or a phthalate buffer solution.

Commercially available $NaClO_2$ (Eastman Kodak) with a chlorite content of 82.3% (major impurity Cl^-) was recrystallized twice from 0.001 M NaOH to give a purity of 99.2% as determined iodometrically. The chlorite stock solutions were prepared and stored as described earlier.[6] Bromide and thiocyanate solutions were prepared by dissolving reagent grade (Fisher) KBr and KSCN in water. The ClO_2^-–Br^- reaction generates significant amounts of Br_2 and interhalogen compounds and was therefore studied in a hood.

The reactor was filled with the input solutions at the highest available pump speed. After a stable state (steady or oscillatory) was reached, the pump speed was stepped down and the new stable state determined. When the minimum pump speed was reached, the process was reversed and the flow rate was increased stepwise in order to probe for possible hysteresis.

Results

ClO_2^-–Br^-. When acidic (0.5 M H_2SO_4) solutions of chlorite and bromide are studied in a closed (batch) system, the reaction is found to be autocatalytic. Mechanisms have been proposed independently by Valdes-Aguilera et al.[11] and Simoyi[12] to explain the course of this reaction involving autocatalysis in bromine formation, in a manner analogous to the well-known chlorite–iodide reaction where iodine constitutes the autocatalytic species. Interhalogen compounds play an important role in these mechanisms.

When feed streams of chlorite, bromide, and sulfuric acid are flowed into a CSTR the system exhibits a wide region of bistability. Figure 1 shows the phase diagram of this system in the chlorite–bromide plane. With increasing $[ClO_2^-]_0$ or $[Br^-]_0$ the bistable domain narrows until at about 0.0125 M $[ClO_2^-]_0$ the high potential steady state bifurcates to an oscillatory one. With increasing flow rate the oscillations give way to the low potential steady state; on lowering the flow rate, however, there occurs hysteresis between the oscillatory and the low potential state in exactly the same manner as in the bromate–iodide oscillator.[13] The range of oscillation in the present system is considerably narrower than in the bromate–iodide system.

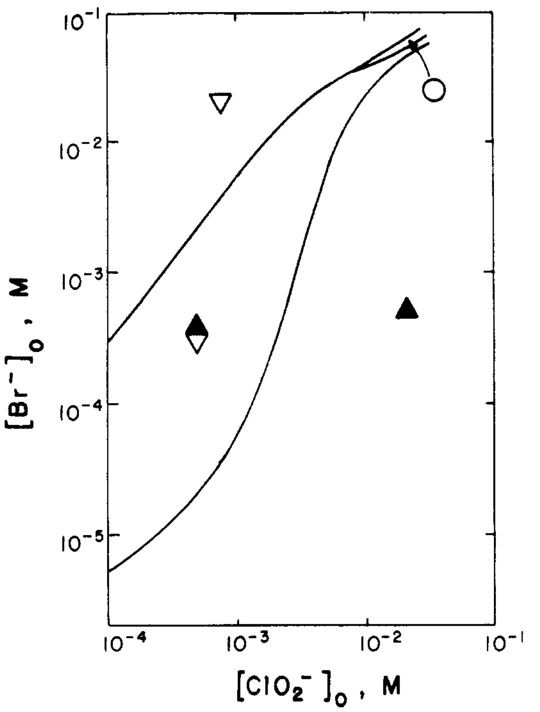

Figure 1. Phase diagram of the chlorite–bromide system in the $[ClO_2^-]_0$–$[Br^-]_0$ plane. $[H_2SO_4]_0$ = 1 M, reciprocal residence time k_0 = 0.003 s^{-1}. Symbols: ▽, low Pt-potential steady state; ▲, high Pt-potential steady state; ◆, bistability; ○, oscillation.

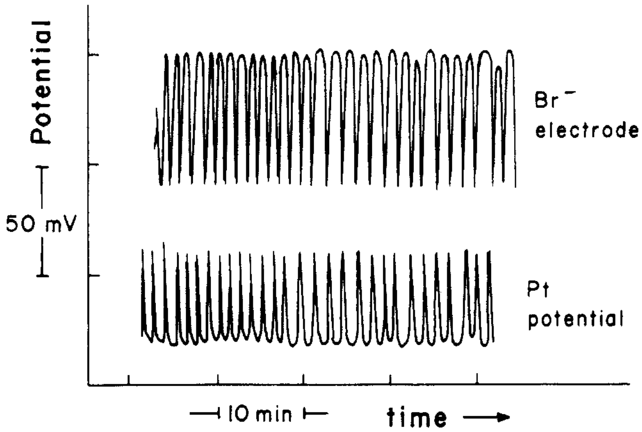

Figure 2. Potential traces of oscillations in the chlorite–bromide reaction. $[ClO_2^-]_0$ = 0.01 M, $[Br^-]_0$ = 0.035 M, $[H_2SO_4]_0$ = 1 M, k_0 = 0.002 s^{-1}.

Traces of the oscillations are shown in Figure 2. It should be noted that reproducing the oscillations in this system is somewhat difficult owing to the narrow domain of oscillation and the extreme sensitivity of the system to the stirring rate.

Figure 3 shows the effect of stirring on the chlorite–bromide system. We have selected a bistable point from the phase space. With increasing stirring rate the region of bistability widens. The effect of stirring is only apparent on the transition from the high potential steady state to the low potential state; the reverse transition remains virtually unaffected. For example, the high potential state is stable up to flow rates of 700 at a stirring rate of 900 rpm. Decreasing the stirring rate to 650 rpm shifts the system into the low potential state at any flow rate above 525.

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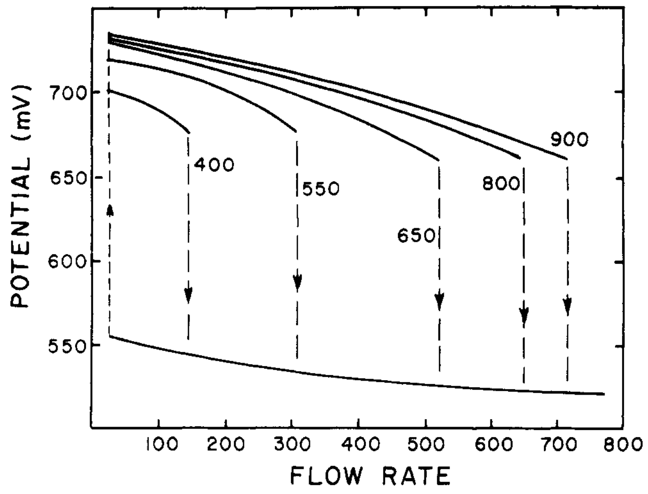

Figure 3. Stirring effects on bistability in the chlorite–bromide system. Numbers on upper solid curves indicate stirring speed in rpm. Flow rates are given as pump setting which is proportional to the reciprocal residence time. Arrows indicate transition. Lower curve identical for all stirring rates. $[\mathrm{ClO_2^-}]_0 = 0.005$ M, $[\mathrm{H_2SO_4}]_0 = 1$ M, $[\mathrm{Br^-}]_0 = 0.015$ M.

Roux et al.[14] first reported that the region of bistability in the chlorite–iodide oscillator was extremely sensitive to the rate of stirring. They observed that the transition from the low iodide steady state to the high iodide state occurred at lower flow rates when the stirring rate was decreased. The transition from the high iodide state to the low iodide state, however, remained unaffected. More recently, Kumpinsky and Epstein[15] performed calculations and experiments on the effect of stirring in the chlorite–iodide and bromate–bromide–manganous oscillators. In the minimal bromate oscillator only the transition from the high bromide to the low bromide state is sensitive to the stirring rate. Using a simple two-compartment reactor model which takes into account partial segregation inside the reactor due to imperfect mixing they obtained qualitative agreement between calculations and experiment in both systems.

The chlorite–bromide reaction behaves with respect to stirring in exactly the same manner as the chlorite–iodide system. In the former reaction, the low Pt-potential state is the high bromide state and the flow branch and the high Pt potential is the low bromide and equilibrium state. As noted above, only the transition from the high potential (equilibrium) state to the low potential (flow) state is affected by stirring, as is the case with the chlorite–iodide system.

Chlorite–Thiocyanate. While the $\mathrm{ClO_2^-}$–$\mathrm{Br^-}$ system possesses a large region of bistability and a rather narrow oscillatory domain, the $\mathrm{ClO_2^-}$–$\mathrm{SCN^-}$ reaction exhibits a broad range of oscillation and a bistable region so small, if it exists, as to defy our efforts to observe it. Figure 4 shows the phase diagram, while typical oscillations are depicted in Figure 5.

The oscillation period in the $\mathrm{ClO_2^-}$–$\mathrm{SCN^-}$ system varies over an enormous range, more than in any other chlorite oscillator. A tenfold change in $[\mathrm{ClO^{2-}}]_0$ changes the period from 10 s to about 30 min. A second unusual feature of this reaction is the apparent absence of bistability. On either side of the oscillatory region (Figure 4) there are two distinct steady states which differ in potential by as much as 200 mV near the middle of the oscillatory region. However, neither changes in flow rate nor chemical perturbations were able to generate the transition from one steady state to another characteristic of bistability. Recently, Burger and Field[16] reported failure to observe bistability in the methylene blue–sulfite oscillator.

The location of the oscillatory region in the chlorite–thiocyanate reaction appears relatively insensitive to stirring rate. The concentration ratios for which the system oscillates are similar to those found in other chlorite–sulfur oscillators. Chlorite is always in excess by a factor of 1.5–2.5.

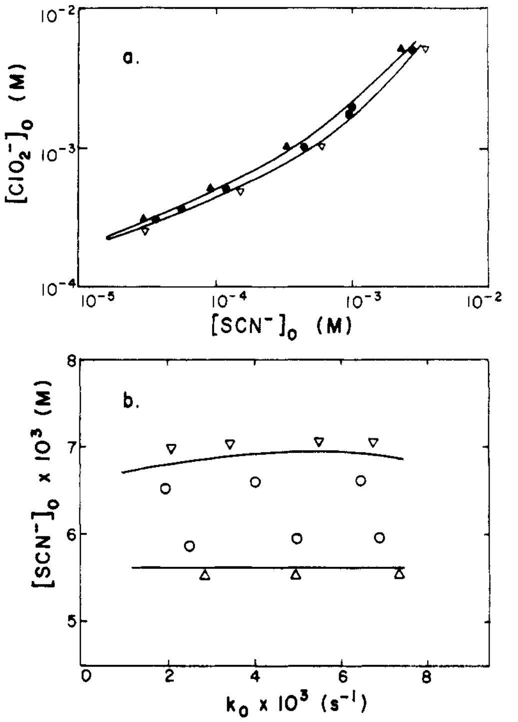

Figure 4. Phase diagrams of the chlorite–thiocyanate reaction: (a) $[\mathrm{ClO_2^-}]_0$ – $[\mathrm{SCN^-}]_0$ plane, pH 2.9, $k_0 = 0.0036$ $\mathrm{s^{-1}}$; (b) $[\mathrm{SCN^-}]_0$–k_0 plane, $[\mathrm{H_2SO_4}]_0 = 0.001$ M, $[\mathrm{ClO_2^-}]_0 = 0.0025$ M, $k_0 = 0.003$ $\mathrm{s^{-1}}$.

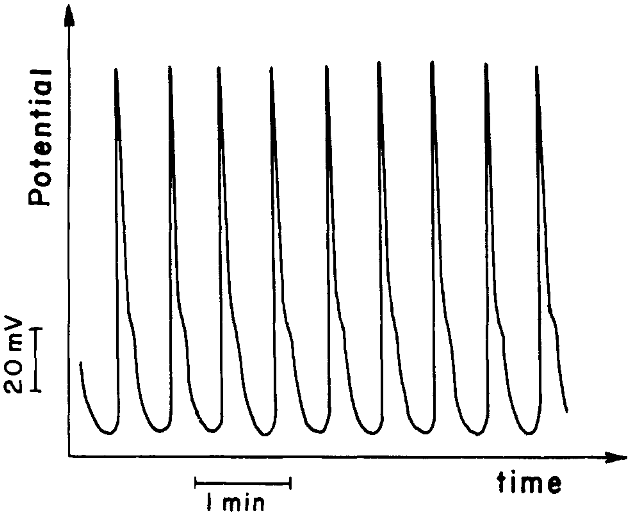

Figure 5. Potential traces of oscillations in the chlorite–thiocyanate reaction. $[\mathrm{ClO_2^-}]_0 = 0.005$ M, pH 3.5, $[\mathrm{SCN^-}]_0 = 0.0025$ M, $k_0 = 0.003$ $\mathrm{s^{-1}}$.

Chlorite–Thiourea Derivatives. Experiments were also performed to test the effect of substitution of the hydrogens in thiourea on the oscillatory behavior found in the $\mathrm{ClO_2^-}$–$\mathrm{SC(NH_2)_2}$ system.[10] Both phenylthiourea (PTU) and tetramethylthiourea (TMTU) do give rise to oscillations. The phase diagrams obtained in these preliminary experiments resemble that of the $\mathrm{ClO_2^-}$–$\mathrm{SCN^-}$ system rather than that of the parent chlorite–thiourea reaction, in that no bistability was found. The oscillations occur with typical constraint values of $[\mathrm{H_2SO_4}] = 0.1$ M, $[\mathrm{ClO_2^-}]_0 = 0.002$–$0.005$ M, [PTU] or $[\mathrm{TMTU}]_0 = 0.001$ M, and $k_0 = (2$–$15) \times 10^{-3}$ $\mathrm{s^{-1}}$.

Discussion

Although one might expect bromide and thiocyanate to show some similarities in their kinetic behavior with chlorite, the resemblance seems to be limited to the fact that both give oscillation. Bromide behaves much like iodide in giving a large area of bistability, relatively narrow region of oscillation, bistability be-

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tween steady and oscillatory states, and marked sensitivity to stirring rate. Thiocyanate shows none of these features.

A mechanistic explanation of the chlorite–bromide oscillations seems within reach given the reactions's similarity to the chlorite–iodide reaction and the success of numerical simulations[11,12] of batch behavior in the chlorite–bromide system. In contrast, very little is known about the ClO_2^-–SCN^- reaction. We did not perform direct experiments to establish its stoichiometry, but by analogy with the bromate–thiocyanate reaction[17]

$$BrO_3^- + SCN^- + H_2O = Br^- + CN^- + SO_4^{2-} + 2H^+ \qquad (1)$$

the following stoichiometry appears reasonable:

$$3ClO_2^- + 2SCN^- + 2H_2O = 3Cl^- + 2CN^- + 2SO_4^{2-} + 4H^+ \qquad (2)$$

The discovery of oscillations in the ClO_2^-–SCN^- system extends the number of known chlorite–sulfur oscillators to three. The systems containing the thiourea derivatives may be considered to be further new examples or merely variations on the parent system. In any case, all known chlorite–sulfur oscillators are anomalous or complex in some fashion, though the ClO_2^-–SCN^- reaction would seem to be the easiest to attack from a mechanistic point of view. In all of these systems, sulfur is present in the 2– oxidation state. This observation suggests that sulfide ion might provide the simplest possible chlorite–sulfur oscillator. While preliminary studies of the ClO_2^-–S^{2-} reaction[18] showed some evidence of oscillation, efforts to reproduce these results have thus far been unsuccessful. It remains to be seen whether this behavior was indeed genuine. Organic compounds containing sulfur in the 2– oxidation state may also be worth exploring as possible partners for chlorite in new oscillators.

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Infrared Spectrum of the Fundamental Vibration–Rotation Band of $^3\Sigma^-$ OH^+

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The fundamental $v = 1 \leftarrow 0$ vibration–rotation band of the $^3\Sigma^-$ OH^+ ion has been observed by using the tunable infrared radiation from a difference frequency system and the velocity modulation technique of detection. The band origin was determined to be $\nu_0 = 2956.3724$ (29) cm^{-1}. The rotational constant B, the centrifugal distortion constant D, and the spin–spin and the spin–rotation constants λ and γ have been determined for the ground and for the first excited states. It was found that the discharge condition for the effective production of OH^+ (and H_2O^+) is very different from that for H_3O^+. The ion–molecule reactions leading to the formation of OH^+ in the discharge are discussed.

Introduction

Infrared spectroscopy of molecular ions using frequency tunable laser radiation sources and discharges has recently been applied to many fundamental molecular ions.[1] Most of the molecular ions studied by this method are protonated ions HX^+ in which a proton is attached to stable molecules and atoms to form closed-shell structures. Because of the high proton affinities of stable molecules and atoms, the protonated ions are often the end products in the chain of molecular reactions in the discharge of H_2:X mixtures.

In this paper we report our application of the same method to the open-shell OH^+ molecular ion which belongs to a different category of ions. The discharge conditions to produce this type of ion abundantly are considerably different from those commonly used for protonated ions. In the discharge described later in detail, the usually strong H_3O^+ lines are barely visible, but the lines of OH^+ and H_2O^+ are clearly observable. We summarize our results on OH^+ in this paper; the spectrum of H_2O^+ will be published later in a separate paper.

The vibration–rotation constants of OH^+ have already been well determined from the detailed study of the optical emission spectrum by Merer and his colleagues.[2] The history and earlier spectroscopic papers on this molecular ion are summarized in the paper. The ground electronic state has the symmetry $^3\Sigma^-$, and therefore a triplet structure is expected. This ion has been detected in comets through the optical spectrum by Fehrenbach and Arpigny.[3] Very recently Saykally and colleagues have observed rotational transitions of this molecule in the far infrared region by laser magnetic resonance.[4] During preparation of this paper we also learned that Dymanus and colleagues have observed the $J = 1 \leftarrow 0$ rotational transition in the submillimeter wave region.[5]

Experiment

A difference frequency laser system developed by Pine[6] was used as the frequency tunable infrared source. A small-bore (4 mm i.d.) water-cooled ac discharge cell with the length of 1 m was used as the absorption cell. A gas mixture of 100:1:1 He:O_2:H_2 at the total pressure of 10 torr gave the best results. Because of the small diameter of the discharge tube, a minimum pressure of ~4 torr was needed to maintain a stable ac discharge. The He:H_2O mixture used by Merer et al.[2] also gave absorption signals in a water-cooled cell and in a liquid-N_2-cooled cell; however, both He:H_2O and He:H_2:O_2 mixtures gave weaker signals at liquid N_2 temperature. The powerful velocity modulation technique introduced by Gudeman, Saykally, and others[7]

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