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Rhett James Barnes and Amitabha Sinha

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Rhett James Barnes and Amitabha Sinha

Department of Chemistry and Biochemistry, University of California-San Diego, 9500 Gilman Drive, La Jolla, California 92093-0314

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The unimolecular decomposition of HOCl is investigated by exciting the molecule to the region of the sixth overtone of its OH stretching vibration $(7 \nu_{OH})$ using overtone–overtone double resonance. The excitation scheme is sufficiently selective to allow preparation of a single angular momentum quantum state within the $7 \nu_{OH}$ vibrational manifold lying $\sim 2500 \text{ cm}^{-1}$ above the dissociation limit. From the measured linewidths associated with the rotational features appearing in the action spectrum, we obtain an upper limit estimate for the dissociation rate of $k_{uni} < 9.4 \times 10^9 \text{ s}^{-1}$ which is substantially slower than that expected on the basis of RRKM theory. The nascent OH fragment product state distribution exhibit strong oscillations which depend on the rotational quantum numbers of the parent HOCl molecule. From the measured energy release associated with the OH fragment, the heat of formation of HOCl is estimated to be $\Delta H_0^0(0 \text{ K}) = -16.7 \pm 0.6 \text{ kcal/mol}$. © 1997 American Institute of Physics. [S0021-9606(97)02633-0]

INTRODUCTION

Hypochlorous acid, HOCl, is an important species in atmospheric chemistry.¹ Consequently, there has been great interest in characterizing the photochemistry² and dissociation dynamics^{3,4} of this molecule from its electronic excited states. Of course, bond cleavage in HOCl can also occur on its ground electronic surface, however, to the best of our knowledge there has been no prior experimental study reported on this phenomena. In this communication we present the first results on the state-selected unimolecular decomposition of HOCl on its ground electronic surface.

As a covalently bonded closed shell triatomic molecule, HOCl offers several attractive features for investigating unimolecular decomposition. In particular, the relatively low density of vibrational states, a readily detectable product fragment, and the presence of a convenient vibrational chromophore (i.e., the high frequency O-H stretch) all make HOCl an attractive system for experimental study. In addition, the large frequency mismatch between the O-H stretching coordinate and the other vibrations of the molecules suggests that vibrational state mixing is likely to be restricted in this system, thus providing an opportunity for observing possible nonstatistical behavior with regards to its dissociation dynamics. Previous state selected unimolecular dissociation studies on other triatomic systems such as NO₂, HCO, and DCO,^{5–7} where the density of vibrational states is also fairly low, have observed a range of dissociation dynamics with HCO being highly mode specific,⁶ NO₂ being statistical on average⁵ and DCO being somewhere in between.⁷

Experimentally the challenge of studying unimolecular reactions on the ground electronic surface lies in the difficulty associated with preparing high energy vibrationaly excited states lying above the dissociation limit. This is particularly true for molecular systems that do not possess accessible bound excited electronic states for use in state preparation schemes such as stimulated emission pumping or internal conversion, the two methods that have been used, for example, to study the unimolecular dissociation of HCO(DCO) and NO₂, respectively. For HOCl, whose low lying excited electronic states are all dissociative, we have used the technique of vibrational overtone-overtone double resonance to access its vibrationally excited levels. This approach is similar to the method developed by Rizzo and co-workers⁸ and involves accessing a high energy vibrational overtone state by breaking up the overall excitation process into two sequential steps. In our case we use two sequential lower order overtone transitions, where as in their original work Rizzo and co-workers used the combination of a fundamental excitation followed by an overtone transition. We have recently demonstrated the utility and feasibility of the overtone-overtone double resonance technique by accessing highly vibrationally excited states of water in the energy range of $\sim 25\ 200\ \text{cm}^{-1.9}$ In the present case application of the double resonance technique to HOCl involves using the idler beam from an OPO to excite ground state molecules to the first overtone level of the OH stretch $(2\nu_{OH})$ around 7050 cm^{-1} and then subsequently using a dye laser to further excite the selected molecules to the target vibrational level corresponding to the $7 \nu_{\rm OH}$ state which lies $\sim 2500 \, {\rm cm}^{-1}$ above the dissociation limit. Monitoring the yield of OH fragments resulting from the unimolecular decomposition as a function of the excitation laser frequency, provides the means for obtaining information about the predissociative final vibrational state and for probing the dissociation dynamics (see Fig. 1).

EXPERIMENT

The details of the experimental apparatus have been described in our earlier work on H₂O and HOBr.^{9,10} We synthesize HOCl by simultaneously flowing water vapor and Cl₂ through two separate ports at one end of a glass column (1.5 cm diameter \times 35 cm length) packed with a mixture of yellow HgO and 6 mm diameter glass beads. The beads allow for a loose packing of the HgO powder and thus insure



FIG. 1. Schematic diagram illustrating the vibrational overtone-overtone double resonance excitation scheme used to initiate unimolecular decomposition of HOCI. The vibrational quantum numbers shown are for the O–H stretching coordinate. The HO–Cl bond dissociation energy is estimated to be $\sim 19 \ 210 \ \mathrm{cm^{-1}}$ (Ref. 14).

uniform flow of reagents through the column. The other end of the column is connected to the glass photolysis cell and the mixture of reactants and HOCl products continuously flows into the cell. The cell is evacuated by a partially throttled mechanical vacuum pump resulting in a total pressure in the cell between $\sim 60-100$ mTorr. Light (~ 11 mJ) from an OPO (Spectra-Physics MOPO 730) which is pumped by the third harmonic of a pulsed Nd:Yag laser excites the HOCl molecules in the region of the first overtone level of the OH stretching vibration $(2v_{OH})$. We pick off a small portion of infrared light from the OPO and pass it through a photoacoustic cell containing water vapor for wavelength calibration. After a delay of ~ 30 ns a separate Nd:Yag-pumped dye laser, operating in the region of 680 nm, further excites the HOCl molecules from the intermediate state to the $7 \nu_{OH}$ vibrational level. The frequency doubled output of a third Nd:Yag pumped dye laser system is used to detect the OH fragments resulting from the unimolecular decomposition by laser induced fluorescence (LIF) through the A - X transition at ~ 308 nm.

RESULTS AND DISCUSSION

The first requirement for implementing the doubleresonance scheme to investigate unimolecular reaction, involves characterization of the intermediate vibrational state. For HOCl, we have examined the $2\nu_{OH}$ vibrational level using the technique of vibrationally mediated photo-



FIG. 2. (a) Action spectrum of the HOCl $2\nu_{OH}$ vibrational state obtained by photodissociating HOCl($2\nu_{OH}$) through electronic excitation using 355 nm light while monitoring the yield of OH(v''=2, N=2) fragments as the vibrational excitation laser frequency is scanned. (b) Action spectrum of the $2\nu_{OH} \rightarrow 7\nu_{OH}$ transition with the IR laser frequency set on the ${}^{P}Q_{2}$ stack shown in (a) while probing the OH(v''=0, N=8, ${}^{2}\Pi_{3/2}$) state resulting from unimolecular dissociation. (c) Action spectrum of the $2\nu_{OH} \rightarrow 7\nu_{OH}$ transition with the IR laser parked on the ${}^{P}Q_{3}$ stack shown in (a) while probing the OH(v''=0, N=8, ${}^{2}\Pi_{3/2}$) state resulting from unimolecular dissociation.

dissociation.¹¹ In these experiments HOCl molecules at room temperature are first vibrationally excited to the 2 ν_{OH} level using infrared light from the OPO and then subsequently photodissociated using UV light at 355 nm from a Nd:Yag laser. Monitoring the yield of a particular quantum state of the OH fragment resulting from the photodissociation, as the frequency of the vibrational excitation laser is varied, generates the action spectrum shown in Fig. 2(a). The spectrum consists of both perpendicular and parallel transitions characteristic of a hybrid band of a near prolate symmetric top and the assignments shown in Fig. 2(a) are based on the earlier work of Cavazza *et al.* using high resolution absorption spectroscopy.^{12(a)} Having determined the location of these spectral features, we are able to implement the second step in the double resonance scheme.

As is evident from Fig. 2(a), the resolution of our OPO $(\sim 0.3 \text{ cm}^{-1})$ is insufficient to resolve individual rotational transitions of the $2\nu_{\text{OH}}$ band in HOCl. However, if we park the OPO on one of the isolated K_a stacks associated with a perpendicular component of this band, for example the PQ_2

stack shown in Fig. 2(a) and then scan the dye laser corresponding to the second step of the double resonance excitation process, we obtain the spectrum shown in Fig. 2(b). This action spectrum corresponds to excitation to the 7 ν_{OH} vibrational level from the selected intermediate state(s) and is obtained by monitoring the yield of $OH(N=8, {}^{2}\Pi_{3/2})$ fragments from the unimolecular dissociation of HOCl as the frequency of the $2\nu_{OH} \rightarrow 7\nu_{OH}$ excitation laser is varied. As is clear from the figure, we are able to resolve individual rotational transitions of this parallel band with our $\sim 0.1 \text{ cm}^{-1}$ resolution dye laser. Thus, even though the resolution of our OPO prevents complete state selection in the $2 \nu_{OH}$ intermediate level, the final rotational states of the $7 \nu_{\rm OH}$ band are cleanly resolved in these experiments allowing a state selective study of the dissociation dynamics. By parking the OPO on various other K_a stacks of the $2\nu_{OH}$ spectrum shown in Fig. 2(a) and then scanning the dye laser, we can effectively decompose $2\nu_{\rm OH} \rightarrow 7\nu_{\rm OH}$ excitation spectrum into its K_a components. Figure 2(c) shows the results of selecting transitions belonging to the ${}^{P}Q_{3}$ stack in the intermediate state.

Although extensive spectroscopic analysis exist for the lower vibrational levels of HOCl,¹² the $7\nu_{OH}$ band has not been previously analyzed. The rotational assignment shown in Fig. 2(b), is based on a analysis using an asymmetric rotor fitting program¹³ and has been subsequently verified using combination differences of the well characterized $2\nu_{OH}$ intermediate state. In these experiments for confirming spectral assignment, we fix the dye laser (corresponding to the second step of the double resonance scheme) on a particular feature of the 7 ν_{OH} band that we are interested in assigning, and then scan the wavelength of the IR laser to determine which states of the $2\nu_{OH}$ level are connected to it through dipole selection rules. The lines appearing in the resulting spectra can easily be assigned using known spectroscopic constants for the $2\nu_{OH}$ level and from this information, the assignment of the spectral feature in the $2\nu_{OH} \rightarrow 7\nu_{OH}$ spectra can then be deduced. From a preliminary analysis of the action spectra, such as the ones shown in Figs. 2(b)-2(c), we have obtained a set of approximate spectroscopic constants for the band origin and rotational parameters of the HOCl³⁵ These are $\nu = 21\ 709.07\ \mathrm{cm}^{-1}, A$ $(7 \nu_{\rm OH})$ band. $= 15.156 \text{ cm}^{-1}$, $B = 0.503 \text{ cm}^{-1}$, and $C = 0.487 \text{ cm}^{-1}$.

An examination of the linewidths associated with the resonances appearing in $K_a = 1$ subband [i.e., Figs. 2(b)] indicates that they are limited by the linewidths of our dye laser ($\sim 0.1 \text{ cm}^{-1}$). For example, the feature indicated by the arrow in Fig. 2(b), which corresponds to the J=12, $K_a=1$, $K_c = 11, 12(7\nu_{\text{OH}}) \leftarrow J = 13, K_a = 1, K_c = 12, 13(2\nu_{\text{OH}})$ resonance, has a linewidth of 0.11 cm^{-1} (FWHM). We are unable to resolve the asymmetry splitting associated with this transition or the splitting due to the Cl^{35}/Cl^{37} isotopes. Within our resolution, the widths of the resonances in the $K_a = 1$ manifold appear to be independent of the J quantum number of the parent molecule spanning a narrow range of values around 0.11 \pm 0.01 cm⁻¹ (FWHM). Taking into account the influence of Doppler broadening and the finite spectral width of the excitation laser, we estimate an upper limit contribution to the linewidth from homogeneous broadening at $\Delta \nu < 0.05 \text{ cm}^{-1}$. This value allows us to place a lower limit on the dissociation lifetime of HOCl from the $7\nu_{\rm OH}$ level at $\Delta t > 1.06 \times 10^{-10}$ s ($\Delta t = 1/2\pi\Delta\nu$). We can compare this result with predictions of RRKM theory where the dissociation rate is given by $k(E) = N^{\sharp}(E - E_0)/h\rho(E)$. In the above expression N^{\sharp} corresponds to the number of open channels at the transition state, h is Plank's constant, ρ is the density of states of the reactant molecule and E_0 is the threshold energy for reaction. As is well known, application of this expression to a barrierless potential, such as in HOCl, is difficult due to the problems associated with locating the transition state and thus calculating $N^{\sharp}(E-E_0)$. Typically in these situations the transition state is determined by applying variational methods to locate the region of the potential energy surface where the reactive flux is a minimum. For our current purposes, however, it suffices to take $N^{\sharp}(E-E_0)$ = 1, which gives a lower limit for the RRKM rate. As we show below, even this lower limit RRKM rate is substantially larger than that obtained from the measurements. Apart from $N^{\sharp}(E-E_0)$, the other quantity required for the rate calculation is the density of states, which using currently available spectroscopic data,^{12(b)} we determine to be ρ =0.2 states/cm⁻¹ at the excitation energy. Using these values in the RRKM expression gives a lower limit estimate for the unimolecular rate of: $k_{\text{RRKM}}(E) > 1/h\rho(E) = 1.5$ $\times 10^{11}$ s⁻¹, which corresponds to a lifetime of 6.7 $\times 10^{-12}$ s. The difference between this lifetime and that estimated from the linewidth measurements suggests that the fundamental assumption of RRKM theory, that energy randomizes on a time scale much faster than the rate of dissociation, appears not to hold for the $7 \nu_{OH}$ vibrational state of HOCl. Incomplete vibrational mode mixing in the molecule is consistent with the fairly regular spectrum observed. We have also tried to determine the dissociation rate of the HOCl($7\nu_{OH}$) level directly by varying the time delay between the excitation and probe lasers, but have found the rate to be faster than the time resolution afforded by our nanosecond laser system.

In addition to measuring the linewidths, we have also examined the reaction dynamics by monitoring the OH fragment internal state distributions resulting from the unimolecular dissociation. Figure 3, shows the product rotational state distribution for the OH ${}^{2}\Pi_{3/2}$ manifold obtained from dissociation of the J=12 state of HOCl($7\nu_{OH}$) for various values of K_a . These measurements clearly reveal that the position and amplitude of the oscillations appearing in the OH product state distribution are strongly dependent on the rotational quantum numbers of the initial state. From the Doppler widths associated with the laser induced fluorescence spectra of the OH fragment, it is possible to obtain an estimate for the heat of formation, ΔH_0^0 of HOCl. So far, we have not determined the branching ratio between the two possible spin-orbit states of the chlorine fragment which are separated by $\sim 882 \text{ cm}^{-1}$. However, if we assume that the highest energy rotational state of the OH fragment that is detected, N=11, correlates *exclusively* with the production of chlorine atoms in their lowest spin-orbit state, the ${}^{2}P_{3/2}$ state, then the linewidth associated with transitions appearing



FIG. 3. OH fragment product rotational state distribution resulting from state selected unimolecular decomposition of HOCl($7\nu_{OH}$) from the J=12angular momentum state for various values of the K_a quantum number. The data is obtained by probing rotational levels in the ground vibrational state of OH using transitions belonging to the $Q_1(N)$ branch.

in the OH LIF spectra allows an estimate of the heat of formation through the following relations: $E_i + h\nu_1 + h\nu_2 - D_0 = E_{rol}[OH(N)] + E_{tran}$, with $D_0 = \Delta H_0^0(OH) + \Delta H_0^0(CI) - \Delta H_0^0(HOCI)$. In the above equations E_i is the energy of the initial rotational state of HOCl from which the double resonance excitation is initiated, $h\nu_1$ and $h\nu_2$ are the photon energies used in the double resonance scheme, $E_{rot}[OH(N)]$ is the rotational energy of the probed OH fragment, E_{tran} is the relative translational energy of the OH+Cl fragments as determined from the linewidth of the probed OH transition, and $\Delta H_0^0(CI)$ and $\Delta H_0^0(OH)$ are the literature values for the heats of formation of the OH and Cl fragments.¹⁴ Applying this equation and using the Doppler linewidths associated with the OH($N = 11,^{2}\Pi_{3/2}$) state, we estimate ΔH_{0}^{0} for HOCl to be -16.7 ± 0.6 kcal/mol in fair agreement with the value reported in the JANAF data base $(-17.1\pm0.5$ kcal/mol).¹⁵ In addition, we note that the small translational energy release observed for the OH(N = 11) state, suggests that *if there is a barrier* along the OH+Cl dissociation coordinate of HOCl, it must be fairly modest as we would expect a substantial fraction of the energy associated with the barrier height to be channeled into relative translation. We are currently examining dissociation of HOCl from the $\delta \nu_{OH}$ vibrational level, which due to its lower energy, will facilitate a more critical examination of the threshold region for reaction.

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