AIP | The Journal of Chemical Physics

Direct measurement of eigenstate-resolved unimolecular dissociation rates of HOCl

M. R. Wedlock, R. Jost, and T. R. Rizzo

Citation: The Journal of Chemical Physics **107**, 10344 (1997); doi: 10.1063/1.474227
View online: http://dx.doi.org/10.1063/1.474227
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/107/23?ver=pdfcov
Published by the AIP Publishing

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1997 issue.

COMMUNICATIONS

Direct measurement of eigenstate-resolved unimolecular dissociation rates of HOCl

M. R. Wedlock
Laboratoire de chimie physique moléculaire (LCPM), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

R. Jost
Grenoble High Magnetic Field Laboratory[a] MPI and CNRS BP 166 F-38042 Grenoble Cedex 9, France

T. R. Rizzo
Laboratoire de chimie physique moléculaire (LCPM), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

(Received 21 August 1997; accepted 8 October 1997)

Double-resonance overtone excitation prepares HOCl molecules in single rovibrational states above the unimolecular dissociation threshold in the ground electronic state. Detecting the OH dissociation fragments allows us to observe which reactant states lie above or below the dissocation threshold and determine that threshold to be 19 290.3±0.6 cm^{-1}. Dissociation rates from single, well-characterized eigenstates of the parent molecule exhibit fluctuations of more than an order of magnitude. © *1997 American Institute of Physics.* [S0021-9606(97)04047-6]

I. INTRODUCTION

The most rigorous tests of unimolecular reaction rate theories come from experiments in which one specifies completely the initial state of the reactant molecule and detects individual state(s) of the products. Such state-to-state experiments have the potential to critically test both *ab initio* calculations of molecular potential energy surfaces as well as techniques for predicting the dynamics on such surfaces. Several groups have measured unimolecular dissocation rates from single eigenstates of a highly excited reactant molecule on the ground potential energy surface, either by linewidth analysis of transititions to quasibound states as in the case of D_2CO,[1,2] HCO[3–5], and DCO,[6,7] or by spectroscopically probing the decay of the excited reactant, as in the of HFCO[8] and CH_3O,[9,10] or by spectroscopic detection of the dissociation fragments as in the case of HN_3.[11,12] One theme that has been emerging from these studies is that at this level of detail, the unimolecular dissociation rates depend on the vibrational character of the reactant state, either in a mode specific manner[8] or from the statistical nature of the highly excited eigenstate.[2,10,13,14]

We report here direct time-resolved measurements of the unimolecular dissociation of HOCl molecules prepared in single eigenstates near threshold with carefully controlled vibrational character and completely defined rotational quantum numbers. By using double-resonance vibrational overtone excitation, we put HOCl molecules in single rotational levels of $6\nu_1$ (OH stretch). The vibrational density of states of HOCl at this energy is approximately 0.1 per cm^{-1},and the overtone spectra presented herein show no perturbations due to coupling to other vibrational levels. We can therefore consider the dissociation process to be the decay of a pure $6\nu_1$ level into the dissociative continuum. We measure the dissociation rate directly by time-resolved laser-induced fluorescence detection of the OH products. Our results indicate that the unimolecular dissociation rates exhibit large fluctuations even with such well-defined vibrational eigenstate preparation.

II. EXPERIMENTAL APPROACH

The experimental approach for these double-resonance overtone spectroscopy experiments, shown schematically in Fig. 1, has been described previously.[15,16] Briefly, an infrared laser pulse, generated by difference frequency mixing the output of a narrowband (0.02 cm^{-1} Nd:YAG pumped dye laser with the single mode output of the YAG in a $LiNbO_3$ crystal, is used to prepare molecules in single rovibrational states containing two quanta of ν_1 (OH stretch vibration). Approximately 15 ns later, a second Nd:YAG pumped dye laster (0.02 cm^{-1} bandwidth) promotes these preselected molecules to single rovibrational states of $6\nu_1$. If the excited rovibrational state is above the energy needed to break the O–Cl bond, the molecule will dissociate to produce OH + Cl. We detect the overtone absorption by monitoring the OH dissociation fragments via laser-induced fluorescence (LIF) in the $A-X$ band using the frequency doubled output of a third Nd:YAG pumped dye laser. The delay between the second and third lasers is variable but typically set to ∼15

---

[a] The Grenoble High Magnetic Field Laboratory is ''Laboratoire conventionne aux universites UJF et INP de Grenoble.''

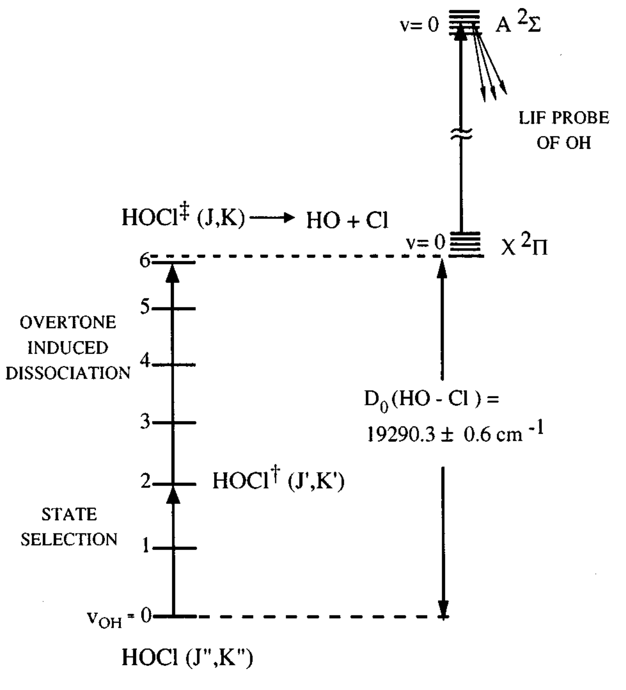

FIG. 1. Energy level schematic for $2\leftarrow0$, $6\leftarrow2$ double-resonance overtone excitation used to access single rovibrational eigenstates in the $6\nu_1$ band of HOCl.

ns. The frequencies of the dye lasers are calibrated using a Burleigh WA-4500 pulsed wave meter. As shown in Fig. 1, we denote the rotational quantum numbers in the ground vibrational state with double primes and those in the intermediate state with single primes. The quantum numbers for the dissociating molecules are unprimed.

Because the $2\nu_1$ band of HOCl is sufficiently sparse,[17] we can pick out single rovibrational states from a low-pressure sample at room temperature. Moreover, the high resolution of the state-selection laser allows us to resolve the chlorine isotopes in the first step, and hence we observe vibrational overtone spectra of single rotational states of a single isotopic species. The data presented herein pertain exclusively to the ^{35}Cl isotope.

We prepare HOCl by simply mixing Cl_2O, which is synthesized according to the method of Schack and Lindahl,[18] with H_2O in a 1:1 ratio. Equilibrium is rapidly attained between these two species and HOCl, with the latter having a fractional concentration of 14%.[19] The resultant mixture flows from a glass bulb through a glass fluorescence cell at approximately 40–50 mTorr as measured by a capacitance manometer. The total OH fluorescence emission passes through a visible-blocking colored glass filter and is imaged onto a UV sensitive photomultiplier tube. The resulting signal is integrated and transferred to a 486 computer via a CAMAC interface.

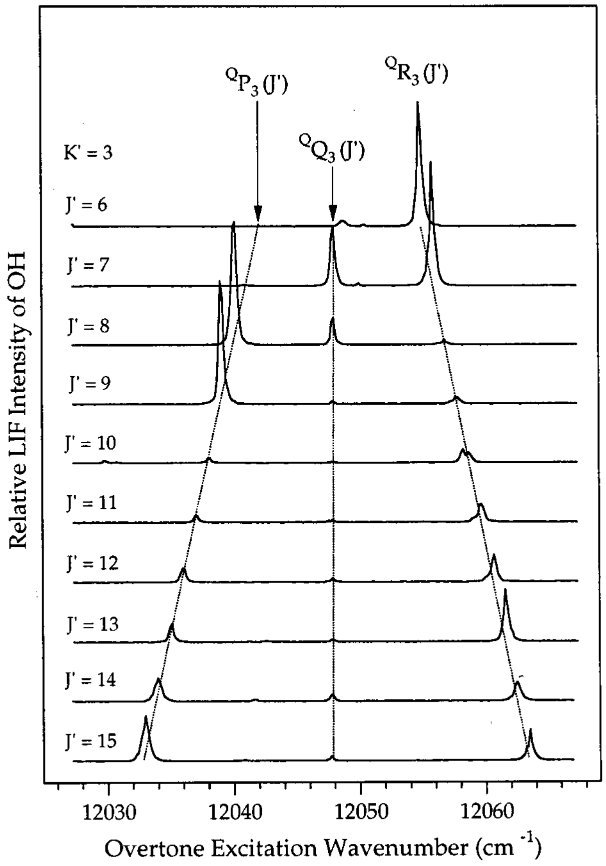

FIG. 2. Series of double-resonance vibrational overtone excitation spectra of the $6\nu_1\leftarrow2\nu_1$ band of HOCl. Rotational states in the $2\nu_1$ intermediate level preselected in the first step have $K'=3$ and $J'=6-15$. The total OH fluorescence is recorded as a function of the frequency of the dissociating laser. The dotted lines indicate the progression of the $^QP_3(J')$,$^QQ_3(J')$, and $^QR_3(J')$ transitions from each intermediate state.

III. RESULTS AND DISCUSSION

A. Photofragment spectra and assignments

Figure 2 shows a series of double resonance vibrational overtone excitation spectra in the $6\nu_1\leftarrow2\nu_1$ band of HOCl obtained by preparing molecules in single rovibrational states of $2\nu_1$ in the first step and then scanning the frequency of the second laser while collecting the total OH fluorescence emission induced by the third laser. For the data shown in this figure, the infrared state selection laser prepares HOCl molecules in $2\nu_1$ with $K'=3$, and J' ranging from 6 to 15, and the laser induced fluorescence probe laser excites the $Q_1(1)$ line of the OH products. Because each of these spectra that terminate on the $6\nu_1$ vibrational level originates from a single rotational state in $2\nu_1$, one observes only three transitions: $^QP_3(J')$,$^QR_3(J')$, and a weaker $^QQ_3(J')$ transition that decreases rapidly in intensity with increasing J'.The fact that there are no $\Delta K=\pm1$ transitions indicates that the transition moment is parallel to the A axis. The simplicity of the spectra testifies to the state selectivity of the double-resonance technique and makes the assignment of the spectra straightforward. Moreover, the lack of splitting of these bands indicates that the final states reached are not perturbed. Although the transition frequencies shown Fig. 2 appear as expected for a parallel band of a prolate symmetric rotor, as is discussed below, the transition intensities are not.

B. Dissociation energy

Because we measure vibrational overtone action spectra by detecting the OH dissociation product of the highly excited molecules, only transitions to final states that are above the dissociation threshold will appear in the spectrum. This allows us to precisely determine the dissociation energy for the O–Cl bond in HOCl. In Fig. 2, the spectra resulting from excitation out of the $K'=3;J'>7$ intermediate states contain all three expected transitions, ${}^{Q}P_3(J')$, ${}^{Q}Q_3(J')$, and ${}^{Q}R_3(J')$, although the transition intensities are not as expected. The spectrum resulting from excitation via the $K'=3;\ J'=7$ intermediate state contains only the ${}^{Q}Q_3(7)$ and ${}^{Q}R_3(7)$ transitions that reach final states with $K=3$ and $J=7$ and 8, respectively. The disappearance of the ${}^{Q}P_3(7)$ transition indicates that the $K=3;\ J=6$ rotational level in the $6\nu_1$ vibrational level is below the dissociation threshold and does not dissociate. We confirm this by measuring the spectrum obtained by excitation via the $K'=3;\ J'=6$ intermediate state in which we observe only the ${}^{Q}R_3(6)$ transition to the $K=3,\ J=7$ final state. We therefore conclude that the dissociation threshold lies somewhere between the energies of the $6\nu_1$ $K=3,\ J=6$ rotational state and the $K=3, J=7$ state.

We determine the dissociation threshold more precisely by measuring spectra in other K manifolds. In the $K=2$ manifold, for example, we find that the dissociation threshold occurs between the $J=14$ and $J=15$ final states. The interleaving of energy levels in the $K=2$ and $K=3$ manifolds allows us to place the dissociation threshold between the energy of the $K=3, J=7$ state (19 290.84 cm -1), which leads to dissociation and the state with $K=2, J=14$ (19 289.66 cm^{-1}), which does not dissociate. We therefore determine the dissociation energy to be 19 290.3±0.6 cm^{-1}. The final state energies are determined by adding the excitation wave number of the second laser to the eigenvalue of the intermediate state, as determined from the infrared spectra of $2\nu_1$ of Cavazza and co-workers.[20]

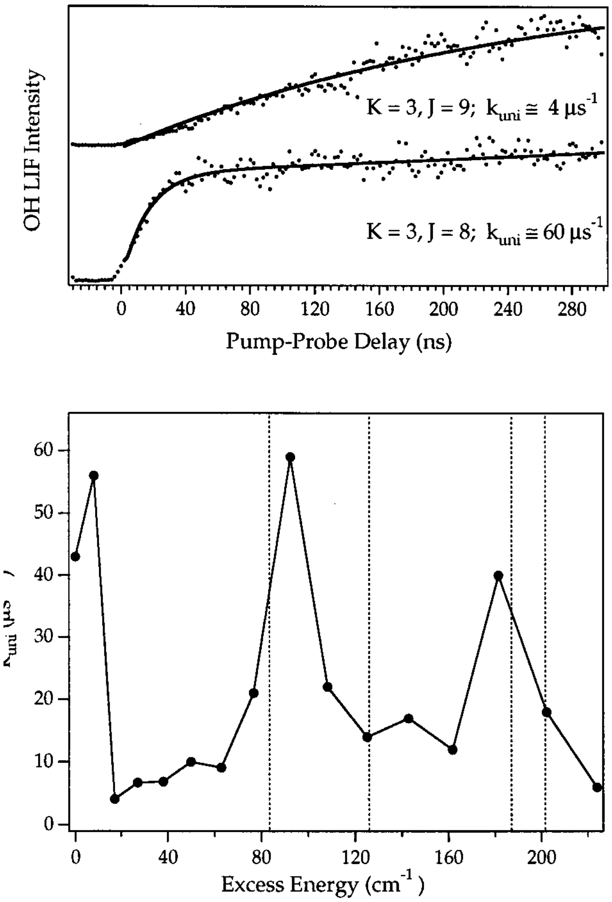

FIG. 3. Dissociation rates of HOCl in the $6\nu_1$ vibrational band. The upper panel shows the change in laser-induced fluroescence from the OH dissociation product as a function of the delay between the overtone pump and LIF probe lasers for the $6\nu_1$ $K=3;\ J=8$ and $K=3;\ J=9$ states of HOCl. Exponential fits to the early portion of the data are shown as solid lines. In the lower panel dissociation rates are plotted versus the amount of excess energy above the dissociation threshold. Rates for final states with $K=3$ and $J=7-22$ are shown. The dotted vertical lines indicate excess energies at which new OH product rotational levels become energetically available. From left to right the dotted lines are, respectively, the energetic thresholds for the ${}^2\Pi_{3/2}(N=2)$,${}^2\Pi_{1/2}(N=1)$,${}^2\Pi_{1/2}(N=2)$ and ${}^2\Pi_{3/2}(N=3)$ OH product states.

C. Dissociation rates

As previously noted, transition intensities in the spectra of Fig. 2 are not as expected for a parallel band of a near prolate symmetric top. For example, the R transition arising from the $K'=3;\ J'=8$ level (Fig. 2) appears to be anomalously weak when compared to the P and Q transitions from the same intermediate state. This results from collecting spectra with a short (~15 ns) delay between the dissociation and probe lasers. If a molecule falls apart slowly compared to this short delay, its intensity will appear smaller than expected. Indeed, the dissociation rate for the $K=3;\ J=9$ final state is substantially smaller than that for the other two states reached via the $K'=3;\ J'=8$ intermediate state (i.e., $J=7$ and $J=8$.) This distortion of spectral intensites occurs throughout the set of spectra shown in Fig. 2. In measurements with longer delays between the overtone pump laser and the probe laser, all the transitions approach their expected intensity.

The upper panel of Fig. 3 shows the early portion of the time evolution of the unimolecular dissociation obtained by fixing the frequencies of the state-selection laser and the overtone excitation laser to produce parent HOCl molecules in two different initial states, fixing the probe laser on the $Q_1(1)$ transition of the OH product, and scanning the time delay between the overtone pump laser and the LIF probe laser. As the HOCl molecule decays producing OH fragments in the probed level, the LIF intensity increases with a rate that reflects the unimolecular dissociation rate of the parent. The total pressure in the fluorescence cell for these experiments was 50 mTorr. At this pressure, the hard sphere gas kinetic collision rate is approximately 5×10^5 per second, corresponding to one collision every 2 μs. Rotational relaxation of parent molecules could conceivably occur as much as 20 times the hard sphere rate or one rotational state changing collision every 100 ns. We therefore estimate dissociation rates by a single exponential fit of the early portion of the curves. These should be of sufficient accuracy to show the strong dependence of the dissociation rate on the initial state of the parent molecule, although it is less accurate for the slower decays. In a full publication to follow, a complete kinetic analysis of the pressure-dependent curves will fit both the rising and falling portions.

From the two time evolution curves shown in Fig. 3, one can see that the unimolecular dissociation rate of HOCl molecules from the state with $K=3$; $J=8$ is about 15 times faster than that at the next higher rotational level, $K=3$; $J=9$. The lower panel shows the disociation rate as a function of energy for the states with $K=3$ and J ranging from 7 to 22. It is clear that over the 225 cm^{-1} range shown in this figure, the dissociation rate varies sharply and nonmonotonically with energy and angular momentum. The sharp changes in dissociation rate are not directly correlated with the availability of new rotational levels for the OH product. Dashed vertical lines in the figure represent the energies at which new OH product rotational states become energetically accessible (see the figure caption).

Not shown on the plot of Fig. 3 are the dissociation rates for HOCl molecules with other K states. We have measured the dissociation rates of HOCl parent molecules from a few states with $K=0$ and find them to be as much as four times faster than the fastest rate measured for molecules with $K=3$. We also observe, however, that $K=0$ lines are perturbed by mixing with two other zeroth-order vibrational states. It is not yet clear whether the higher rates in $K=0$ are evidence of an inverse dependence on the K quantum number or the result of mixing with other vibrational modes that couple more strongly to the dissociative continuum. If the latter is true, the variations that we observe at $K=3$ might result from small components of other vibrational states with intensities too small for us to observe spectroscopically but that dissociate significantly more rapidly than the pure $6\nu_1$ eigenstates. Measurements in progress on the other K manifolds will help clarify the dependence on K as well as the effect of vibrational state mixing.

IV. CONCLUSIONS

Double-resonance vibrational overtone excitation allows us to obtain eigenstate-resolved spectra of molecules in highly excited vibrational states. By applying this technique to the HOC1 molecule we precisely determine the dissociation energy for the O–Cl bond to be 19 290.3±0.6 cm^{-1}. Measurements of the dissociation threshold for different K manifolds at a range of J values are consistent, implying that centrifugal barriers to dissociation do not have a significant impact on our determination.

We also directly measure unimolecular dissociation rates for single, well-characterized eigenstates of HOCl lying near the dissociation threshold. These measurements show wide variations in the dissociation rate over a range of 225 cm^{-1} and variations of as much as a factor of 15 for states differing in J by only one. These fluctuations do not vary monotonically with increasing energy and do not directly depend on the opening of new product channels. Our initial measurements show a strong negative K dependence to the dissociation rate. There is also some evidence of an increase in the dissociation rate for states that have mixtures of other zeroth-order vibrational modes.

With eigenstate-resolved unimolecular dissociation measurements, a molecule as small as HOCl should provide critical tests both of calculations of potential energy surfaces as well as of the dissociation dynamics on such surfaces.

ACKNOWEDGMENTS

We gratefully acknowledge the support of the École Polytechnique Fédérale de Lausanne (EPFL) and the Fonds National Suisse through Grant No. 20-45808.95. Professor R. Jost would like to particularly thank the EPFL for a visiting professorship that supported his stay in Lausanne during which this work was performed. We also thank Arnaud Allanic for providing us with Cl_2O from which we synthesized HOCl and L. Fusina for providing the transition frequencies and vibrational term values for $2\nu_1$.

[1] W. F. Polik, D. R. Guyer, and C. B. Moore, J. Chem. Phys. **92**, 3453 (1990).
[2] W. F. Polik, D. R. Guyer, W. H. Miller, and C. B. Moore, J. Chem. Phys. **92**, 3471 (1990).
[3] G. W. Adamson, X. Zhao, and R. W. Field, J. Mol. Spectrosc **160**, 11 (1993).
[4] D. W. Neyer, X. Luo, I. Burak, and P. L. Houston, J. Chem. Phys. **102**, 1645 (1995).
[5] J. D. Tobiason, J. R. Dunlop, and E. A. Rohlfing, J. Chem. Phys. **103**, 1448 (1995).
[6] C. Stock, X. N. Li, H. M. Keller, R. Schinke, and F. Temps, J. Chem. Phys. **106**, 5333 (1997).
[7] H. M. Keller, M. Stumpf, F. Schroder, C. Stock, F. Temps, R. Schinke, H. J. Werner, C. Bauer, and P. Rosmus, J. Chem. Phys. **106**, 5359 (1997).
[8] Y. S. Choi and C. B. Moore, J. Chem. Phys. **97**, 1010 (1992).
[9] A. Geers, J. Kappert, F. Temps, and J. W. Wiebrecht, J. Chem. Phys. **99**, 2271 (1993).
[10] S. Dertinger, A. Geers, J. Kappert, J. Wiebrecht, and F. Temps, Faraday Discuss. Chem. Soc. **102**, 31 (1995).
[11] B. R. Foy, M. P. Casassa, J. C. Stephenson, and D. S. King, J. Chem. Phys. **90**, 7037 (1989).
[12] B. R. Foy, M. P. Casassa, J. C. Stephenson, and D. S. King, J. Chem. Phys. **92**, 2782 (1990).
[13] W. H. Miller, R. Hernandez, C. B. Moore, and W. F. Polik, J. Chem. Phys. **93**, 5657 (1990).
[14] R. Hernandez, W. H. Miller, C. B. Moore, and W. F. Polik, J. Chem. Phys. **99**, 950 (1993).
[15] B. Kuhn, O. V. Boyarkin, and T. R. Rizzo, Ber. Bunseges. Phys. Chem. 101, 339 (1997).
[16] X. Luo and T. R. Rizzo, J. Chem. Phys. **94**, 889 (1991).
[17] F. Cavazza, G. D. Lonardo, R. Escribano, L. Fusina, P. C. Gome, and J. Ortigoso, J. Mol. Spectrosc. **159**, 395 (1993).
[18] C. J. Schack and C. B. Lindahl, Inorg. Nucl. Chem. Lett. **3**, 397 (1967).
[19] M. -L. Junttila, W. J. Lafferty, and J. B. Burkholder, J. Mol. Spectrosc. **164**, 583 (1994).
[20] L. Fusina (personal communication).