

# The interaction of O(1 D 2) with HCI: The initial vibrational distributions in the OH(2 $\Pi$ ) produced by chemical reaction, and the HCI(1 $\Sigma$ +) produced by E–V energy transfer

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# The interaction of $O(^{1}D_{2})$ with HCI: The initial vibrational distributions in the OH(<sup>2</sup> $\Pi$ ) produced by chemical reaction, and the HCl(<sup>1</sup> $\Sigma$ <sup>+</sup>) produced by E–V energy transfer

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The initial vibrational distributions in both energetically accessible channels of the reaction between  $O({}^{1}D)$  atoms and HCl molecules are reported. The measurements were made using very fast time-resolved Fourier transform spectroscopy to observe the emission spectra of the products before their vibrational populations could be altered by collisional relaxation. Both the OH from the reaction and the HCl created in the E-V energy transfer process have strongly inverted vibrational distributions. The cross section of the former is found to be about 20 times larger than that of the latter. Although spin forbidden, the E-V process is fast, due to the fact that the  ${}^{1}A$  " and  ${}^{3}A$ " surfaces of the HOCl intermediate are nearly energetically degenerate over a large region of configuration space. The results suggest that the dynamics of the interaction are dominated by the relatively slow O-Cl collision. The rapid motion of the H atom, in response to changes in the potential created by the motion of the heavier atoms, permits the system to sample the singlet-triplet intersection many times during the collision. OH rotational deactivation is very fast in this system; the average probability for rotational energy transfer in the v' = 3 level is more than four times larger than the gas kinetic collision probability. The time evolution of both vibrational distributions is also reported, and fast V-Venergy transfer from vibrationally excited OH to ground state HCl is observed.

## **I. INTRODUCTION**

The substantial chemical and photochemical stability of HCl make it an ideal sink for chlorine in most parts of the atmosphere<sup>1</sup>; and this acts to offset the potentially damaging effect of chlorine-releasing chemicals, such as the chlorofluorocarbons, particularly in that part of the ozone layer below about 30-35 km. Above this altitude, however, solar photodissociation of ozone produces  $O({}^{1}D_{2})$  atoms, which react with HCl, releasing OH radicals and Cl atoms:

$$O({}^{1}D_{2}) + HCl \rightarrow OH(v' \leq 4) + Cl,$$
  

$$\Delta H_{0}^{0} = -185.8 \text{ kJ/mol.}$$
(1)

Because both OH and Cl are involved in separate reactions which consume ozone, a single occurrence of this reaction can initiate two catalytic cycles (the Cl/ClO cycle and the  $OH/HO_2$  cycle), each of which removes a molecule of ozone and regenerates the reagent radical on each occurrence of the cycle. Careful studies of the kinetics,<sup>2</sup> temperature dependence,<sup>3</sup> and branching ratios<sup>4</sup> in the associated reactions:

$$O({}^{1}D_{2}) + HCl \rightarrow O({}^{3}P) + HCl(v' \leq 5),$$
  
 $\Delta H_{0}^{0} = -188.3 \text{ kJ/mol},$  (2)

- - - -

and

.

$$O({}^{1}D_{2}) + HCl \rightarrow H({}^{2}S) + ClO,$$
  

$$\Delta H_{0}^{0} = -25.1 \text{ kJ/mol},$$
(3)

have determined that the rate of removal of  $O(^{1}D_{2})$  by HCl

is very high:  $1.5 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature-and that about two-thirds of this removal is via reaction (1).

Since both the Cl/ClO and the OH/HO<sub>2</sub> cycle are very important to the overall ozone balance, and since the rate constant of reaction (1) is large, it is imperative to understand the operation of this system of reactions in detail. The most important information in this regard, of course, is the kinetics of the major channels accessible to the reagents at the ambient temperature. After the total rate constants have been measured, it becomes most important to determine the energy partitioning behavior of these channels, because the fate of their products in subsequent reactions depends to a large extent upon their state of excitation. It has been shown that the rates of reactions involving both OH<sup>5</sup> and HCl<sup>6</sup> may be strongly enhanced by vibrational excitation. Furthermore, the vibrationally excited species can undergo certain reactions which are not energetically accessible to the ground state reagents. Their reactions with ozone exemplify this:

$$OH(v = 3) + O_3 \rightarrow O(^{3}P) + OH(v = 0) + O_2,$$
 (4)

$$OH(v = 1) + O_3 \rightarrow H + 2 O_2,$$
 (5)

$$HCl(v = 3) + O_3 \rightarrow Cl + OH(v = 0) + O_2$$
 (6)

become energetically accessible at the indicated vibrational levels. Note that in the last reaction HCl normally considered a stable sink for Cl atoms, is in fact responsible for the simultaneous initiation of both the Cl/ClO and OH/HO<sub>2</sub> catalytic cycles, thus vividly demonstrating the necessity to consider reagent excitation when assessing the potential influence of atmospherically important reactions.

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Only two experimental studies related to the dynamics of reaction (1) have been carried out. That the OH product is vibrationally excited was inferred from the results of early flash-photolysis experiments.<sup>7</sup> Laser induced fluorescence measurements, carried out much later,<sup>8</sup> established that there is strong inversion in the rotational distributions of the OH(v' = 0) and OH(v' = 1) products, and provided an estimate that the population ratio P(v' = 1)/P(v' = 0) is about 1.5, based on an extrapolation of the rotational surprisal plots, thus giving support to the earlier suggestion of product vibrational excitation. These results were reproduced very closely in a quasiclassical trajectory study,<sup>9</sup> which went on to predict that the complete vibrational distribution, when measured, would be found to peak at OH(v' = 2-3).

These partial product energy distributions are similar to the corresponding partial distributions created by the energetically and kinematically similar reaction  $O({}^{1}D_{2})$  $+ H_2 \rightarrow OH(v') + H$ , and the conclusion was drawn from this early work, that in both cases, the substantial rotational inversion arises from the dissociation of an intermediate (HOCl or HOH) which is formed in a highly excited level of the bending vibrational mode by the insertion of the  $O({}^{1}D_{2})$ atom into the molecular bond. The substantial conversion of the bending vibration into rotation was taken to indicate that dissociation occurs before the exoergicity can be completely randomized among the other product modes. This simple, essentially casual, picture of the dynamics of these reactions was challenged recently in work based on Monte Carlo simulations of the  $O(^{1}D_{2}) + H_{2}$  reaction, <sup>10-13</sup> which reproduced both the rotational and angular distributions of the OH, and showed that the rotational inversions are the consequence of angular momentum constraints, and do not imply specificity in the dynamics due to any features of the potential energy surface. Although this analysis has not yet been carried out on the  $O(^{1}D_{2})/HCl$  system, the similarities between the energy distributions of the two reactions suggest that the rotational inversion in this case may have the same origin as well.

The success of the Monte Carlo simulation-an essentially statistical calculation-in reproducing the rotational and angular distributions of the  $O({}^{1}D_{2})/H_{2}$  reaction might suggest that the energy partitioning in the reaction itself is also statistical. This conclusion is not warranted, however. The calculation obtained rotational inversion only for certain choices of the location and height of the exit-channel centrifugal barrier, together with the normal angular momentum conservation constraints.<sup>12,13</sup> Neither of these conditions requires that the reaction intermediate have a long lifetime or that the reaction excergicity be equally shared among all energetically accessible product modes, both of which are essential characteristics of statistical energy partitioning. Furthermore, the symmetrical (forward-backward) experimental angular distribution<sup>14</sup> implies only that either of the O-H bonds in the H-O-H reaction intermediate breaks with equal probability.

The determination of statistical, as opposed to casual, reaction dynamics may be made unequivocally on the basis of the product vibrational distribution. In the case of the  $O({}^{1}D_{2})/H_{2}$  reaction, the OH vibrational distribution has

been shown to be more excited than the statistical one,<sup>15-17</sup> a conclusion which is confirmed by the observation of a nonstatistical OH/OD branching ratio in the isotopically analogous reaction of  $O({}^{1}D_{2})$  with HD.<sup>18</sup> Extensive analysis of the  $O({}^{1}D_{2})/H_{2}$  system indicates that the reaction dynamics involve the insertion of the  $O({}^{1}D_{2})$  into the H<sub>2</sub> bond, followed by the dissociation of the H–O–H intermediate within, on the average, one or two vibrational periods, before the reaction exoergicity can be equally shared among the rest of the product degrees of freedom. This picture, which is essentially that suggested by the original laser induced fluorescence measurements, has been confirmed by several sophisticated dynamical calculations,<sup>19–22</sup> carried out on highly accurate potential energy surfaces.<sup>21,23–25</sup>

Only one dynamics calculation has been carried out on the  $O(^{1}D_{2})/HCl$  system<sup>9</sup>; it used an analytical fit to an *ab* initio potential.<sup>26</sup> The analytical potential was artificially modified to eliminate the effects of the surface intersections which result from the fact that the HOCl intermediate correlates adiabatically with two possible dissociation limits via several potential energy surfaces which are energetically accessible to room temperature reagents. [See Ref. 22 for an extensive discussion of this as it relates to the  $O(^{1}D_{2})/H_{2}$ problem.] In addition, a second artificial adjustment was made to the energy of its entrance channel to account for the fact that the overall excergicity of the Cl + OH channel in the purely ab initio surface is too large by 0.4 eV. As a result of these approximations, the shape of this analytical potential in the reagent entrance channel is not correct; and it cannot represent certain features of the reaction which may be important to the product energy distributions.<sup>22</sup>

In spite of these difficulties, the dynamical calculation based on this analytical surface achieved very close agreement with the only experimental results which had been measured at the time, the inverted rotational distributions in the OH v' = 0 and v' = 1 levels, and the estimated population ratio: P(v'=1)/P(v'=0) = 1.5. In addition, it predicted that the OH vibrational distribution would peak at about the v' = 2-3 level and the angular distribution would be slightly forward peaked. Although it thus predicted highly nonstatistical product energy distributions, the calculation found the lifetime of the HOCl intermediate from which they originate to be very long, about  $5 \times 10^{-13}$  s, a lifetime which should be more than adequate to permit the randomization of the reaction excergicity. These contradictory results show that the dynamics of this process must be quite unusual; and it is clear that the existing information (both experimental and theoretical) is inadequate to provide a description of the reaction. Accordingly, we have measured the complete product vibrational distributions for both reactions (1) and (2) using a novel implementation of timeresolved Fourier transform spectroscopy recently developed in this laboratory.<sup>27,28</sup> We find that the OH(v') distribution created by reaction (1) is strongly inverted and peaks sharply in OH(v' = 3). This agrees qualitatively with the predictions of the dynamical calculation, but the experimental distribution is much narrower and more sharply peaked than the calculation suggested. In addition, we have measured the initial vibrational distribution created by the electronic to

<sup>55.33.16.124</sup> On: Thu, 27 Nov 2014 19:01:24

vibrational energy transfer process, reaction (2). We find it to be strongly inverted as well. It peaks in HCl(v' = 4), at a level having almost exactly the same energy as the level at which the OH vibrational distribution peaks. In the following, we shall first describe the present configuration of the time-resolved Fourier transform experiment, which has been substantially developed and improved since our original description of it,<sup>28</sup> then we shall present the results of our measurements on the  $O({}^{1}D_{2})/HCl$  system and discuss their implications for its reaction dynamics.

### **II. EXPERIMENT**

The vacuum apparatus and optical configuration used in the present experiments have been described previously.<sup>28</sup> Ozone is generated in a 20 kV-60 Hz ac discharge run at - 80 °C. It is stored on Si gel, also cooled to - 80 °C, until required by the experiment. Prior to use, the ozone storage trap is evacuated to a pressure less than 1 Torr (an order of magnitude lower than the equilibrium  $O_3$  vapor pressure on Si gel at -80 °C) for a period of about 1/2 h to 1 h in order to ensure that all residual oxygen is removed. During the experiment, the ozone and HCl flow separately into the reaction chamber (a 25 cm diameter by 25 cm high stainless steel cylinder) and are mixed efficiently at its entrance. The beam from a KrF excimer laser passes through the gas just below the mixing point, irradiating a well-defined volume having a 2 by 1.5 cm cross section, and dissociating part of the  $O_3$ , thus creating  $O(^{1}D)$  atoms. The reaction chamber is evacuated, through a slide valve and cryobaffle, by a 38 cm diffusion pump. The slide valve is adjusted to maintain a total pressure of 10-20 mTorr (composed of equal partial pressures of HCl and  $O_3$ ) in the reaction volume while maintaining an adequate flow to ensure the complete evacuation of the irradiation zone between laser shots.

The  $O(^{1}D)$  atoms are created on the time scale of the laser pulse (about 10 ns) which is instantaneous with respect to subsequent processes. The rate constant for reaction (1) is approximately gas kinetic, and the rates of some of the energy-transfer processes involving the product OH are also nearly this fast. Consequently, the observations must be time resolved on a single-collision basis if the initial OH energy distribution, unperturbed by subsequent collisional energy transfer, is to be determined. The collision time, at a total pressure of 20 mTorr in a room-temperature gas, is approximately 5  $\mu$ s, and this sets the time-resolution necessary for the experiment. In addition to this time resolution it is also necessary to have very sensitive detection of the emission signals, since the product OH has very small infrared transition probabilities (about  $12 \text{ s}^{-1}$  in the  $v = 1 \rightarrow 0$  band<sup>29</sup>) and is present at very low concentration, about  $10^{-5}$ - $10^{-6}$  Torr in the present experiments.

We have previously developed a time-resolved Fourier transform spectrometer designed to carry out such measurements.<sup>27,28</sup> The original version of this instrument was produced simply by using a microprocessor to trigger the photolysis laser synchronously, and in advance of, the data acquisition cycle of a commercial Fourier transform spectrometer. The operation of the commercial machine was not modified in any way in this implementation, but as a result, the achievable time resolution was limited to about 10  $\mu$ s. We have subsequently developed a stand-alone system which carries out not only the timing functions but also the data acquisition as well. Using this instrument, we can measure up to 128 time-delayed spectra, each with a time resolution of 10 ns, for a single excitation event. The initial time delay (the time between the excitation event and the observation of the initial spectrum) may be made arbitrarily short. For the present experiments, since the rise time of the detector (cooled InSb) and preamplifiers is about 2  $\mu$ s, and the collision time is about 5  $\mu$ s, the observations were made on a microsecond time scale. The first data point is taken just before the laser is triggered, in order to provide a background spectrum. Each recorded data point is normalized for laser intensity during the data acquisition.

The new time-resolved system thus replaces the commercial instrument's computer and data acquisition system. The interferometer control (scan velocity, optical retardation, etc.) is done in hardware. The time-delayed interferograms are stored separately in the system memory (4 Mbyte) for subsequent processing. We emphasize that in this system, as in the earlier version, all time delays are recorded on each transient. Therefore, no rearrangement of the interferogram points is necessary to achieve the time resolution. The only mathematical operation carried out on the data prior to Fourier transformation is the coaddition of the interferograms observed at a specific time delay in successive interferometer scans. This data processing prevents any spectral artifacts of the kind which have been observed in other implementations of time-resolved Fourier transform spectroscopy.30,31

The chief noise source in these experiments arises from the pulse-to-pulse variation in the photolysis laser power. In the present experiments, the laser (a modified Lumonics 860T excimer) was being operated at 330 Hz, a substantially higher frequency than that for which it was designed, and this variation amounted to 10%-20%. To correct for this, the laser power was monitored using a photomultiplier, and the data were normalized for this variation.

The data for this entire study were recorded in experiments which required a total of 5–10 h of signal-averaging time. This involved the collection and coaddition of approximately 500 interferograms for each time delay. These were transformed and the resulting spectra were corrected for detector sensitivity and transmission of the optical components in the usual way. The populations of the emitting levels were computed from the known Einstein transition probabilities for  $OH^{29}$  and HCl.<sup>32</sup> The population of each vibrational level was obtained by summing the populations of its rotational levels, all of which were recorded at a resolution of 0.4 cm<sup>-1</sup>.

#### **III. RESULTS**

We shall report data which were recorded at times corresponding to 4, 6, 13, and 18 gas-kinetic collisions after creation of the  $O(^{1}D)$  atoms. The spectrum recorded at four gas kinetic collisions is shown in Fig. 1. The relative intensi-



FIG. 1. The product emission spectra recorded at a time corresponding to four gas kinetic collisions after the reaction.

ties of the HCl and OH spectra show that the major channel in the process is the reaction to form OH. Taking into account the wavelength dependence of the detector sensitivity and the respective Einstein transition probabilities these spectra show that the ratio of the reactive cross section [reaction (1)] to that of the electronic-to-vibrational energy transfer process [reaction (2)] is  $18 \pm 6$ :1, in satisfactory agreement with a previous measurement which obtained  $12 \pm 8$ :1 for this branching ratio.<sup>4</sup>

In Fig. 1, the rotational populations of the OH emitters in the most-populated level, v' = 3, correspond to a Boltzmann distribution at 360  $\pm$  50 K, and those of the v' = 2 and v' = 1 levels are also Boltzmann at temperatures slightly above that of the  $O_3$  and HCl (300 K). The Boltzmann shapes of the observed rotational distributions indicate that this degree of freedom has been substantially relaxed in gas phase collisions before the observation is made (vide infra). The enhanced OH rotational temperatures thus imply that the inflowing gases are heated slightly in collisions with surfaces of the reagent inlet apparatus which, in turn, are heated by the considerable deposition of laser energy in the chamber. Although this implies that the average reagent temperature is somewhat higher than 300 K, the small amount of additional energy which this contributes to the collision (0.8 kJ per 100° temperature increase) is inconsequential to the overall process.

Laser induced fluorescence measurements on this system<sup>8</sup> reported strongly inverted rotational distributions in the OH(v'=0) and (v'=1) levels. The maximum in the v' = 0 rotational distribution (the only one which could be measured completely using LIF) was reported to occur near the highest energetically accessible level, and the partial rotational distribution reported for the v' = 1 level had a similar shape. Thus we conclude that the thermal rotational distributions recorded in the first observation (at four gas kinetic collisions) in the present work indicate that this large rotational inversion has been almost completely thermalized before this observation was made. This implies that the rotational relaxation rates are very large. For example, if the rotational distribution in v' = 3 is similar in shape to that in v' = 0 (as implied by the data from Ref. 8), the maximum in the initial distribution would occur at about J' = 18. The maximum in our data for  $\langle Z_{GK} \rangle = 4$  is at J' = 2, indicating that an average of four rotational quanta are removed per gas kinetic collision. Furthermore, since this cross section increases with decreasing energy gap,<sup>33</sup> the rate for the lower rotational states must be even larger than this. An average rotational energy transfer cross section which is four times gas kinetic is not unreasonable for this system, however. The important collision partners in the relaxation are HCl and  $O_3$ . In addition to the open-shell interactions which OH would undergo with these molecules, rotational deactivation will be enhanced by the transient formation of hydrogen bonds (with  $O_3$ ), and by strong dipole-dipole interactions (with HCl). Bimolecular rate constants for rotational energy transfer ranging from 2.5 to 13 times gas kinetic, for energy defects of 758 and 76  $cm^{-1}$ , respectively, have been measured for HF,<sup>34</sup> and average values on the order of five times gas kinetic have been measured for H<sup>35</sup>Cl/HCl collisions.<sup>35</sup> Multiquantum transitions are also known to be important in this process.35

It has been suggested in connection with similar measurements on the  $O(^{1}D_{2}) + H_{2}$  reaction<sup>36</sup> that there may be an unusual rotational dependence of the OH Einstein transition probabilities for  $\Delta v = -1$  processes, such that the vibrational emission probabilities decrease to very small values for the high rotational states. If this were the case, measurements such as ours would be unable to detect the emissions from the high rotational states and would therefore obtain erroneous vibrational distributions for reactions which create OH with high rotational excitation. The transition probabilities used in the analysis of the data from the present experiments do not show such a rotational dependence, however.<sup>29</sup> To the contrary, they increase with rotational excitation up to the maximum rotational level for which they were reported  $[J = 21/2 \text{ in the OH}(^2\Pi_{3/2})]$ state]. If this dependence is correct, therefore, populations in the higher rotational states will actually yield greater emission intensities than equal populations in the lower states. Although the OH dipole moment function (and hence the transition probabilities) are extremely difficult to calculate, nevertheless the very high-level ab initio computation, which yielded the transition probabilities used here, is unlikely to have obtained a rotational dependence which is qualitatively incorrect. We believe, therefore, that there is no unusual rotational dependence of the A factors or hidden populations in the high rotational states. We have, however, estimated the maximum distortion to our results which could result from residual population in the higher rotational levels by measuring the noise at the location of each of the higher-J transitions (where no signal is observed) and using this, with a smooth extrapolation of the A factors, to estimate the maximum population in each vibrational level which would be missed by the emission measurement if all higher rotational states were populated and their emission had a signal-to-noise ratio of 1. This yielded the result that no population would be missed in the v' = 4 level; 6% of the v' = 3 population would be missed and about 20% of the v' = 2 population. These results were then used to calculate upper-limit error bars for the initial vibrational distribution.

The vibrational populations of the OH levels created by reaction (1) (determined from the observed transitions) and their evolution with time are shown in Fig. 2. In the figure,  $\langle Z_{GK} \rangle$  gives the average number of gas kinetic colli-

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 $O(^{1}D_{a}) + HCl \rightarrow OH(v') + Cl$ 



FIG. 2. The time evolution of the OH vibrational distributions created in reaction (1).  $\langle Z_{GK} \rangle$  gives the average number of gas kinetic collisions suffered by the OH before the observation.

sions which the OH has suffered before the time of the observation, and the upper-limit error bars, estimated as described above, are shown on the  $\langle Z_{GK} \rangle = 4$  data.  $\langle Z_{GK} \rangle$  is calculated from the measured partial pressures using an average collision diameter (3 Å) and assuming that the OH is translationally thermalized on its first gas-kinetic collision. As a result of local heating in the reaction zone and variations in the collision diameters, the values of  $Z_{GK}$  are approximate; but nevertheless they are correct within a factor of 2.

The earliest observation in Fig. 2, that for which  $\langle Z_{\rm GK} \rangle = 4$ , shows that the initial vibrational distribution created by reaction (1) is strongly inverted. The maximum energetically accessible vibrational level is v' = 4, and the initial population of this level is nearly as large as that of the maximum populated level, v' = 3. This distribution does not represent the earliest-possible observation, and hence may have suffered some vibrational relaxation, especially in view of the rapid relaxation of the distributions taken at later times. Although it would be desirable to attempt to correct for this small amount of residual relaxation, by extrapolating backward to the time corresponding to  $\langle Z_{GK} \rangle = 0$ , we do not believe that such an extrapolation provides quantitative information, for several reasons. First, the population of each level depends, in principle, on those of several others, at least on those of the two immediately adjacent ones. The extrapolation, therefore, is not linear. Furthermore, the experimental uncertainty, from the upper-limit error bars described above, and from the normal experimental noise, makes the extrapolation depend upon a range of values, rather than a series of well-defined points. Consequently, we can say only that extrapolation of the present data to  $\langle Z_{\rm GK} \rangle = 0$ indicates that the initial, unrelaxed, distribution has virtually no population in the v' = 1 and 2 levels, whereas levels v' = 3 and 4 have approximately equal populations. As usual, since this is an emission measurement, we have no information at all about the population of v' = 0. These data, taken together with the partial rotational distributions determined by laser induced fluorescence,<sup>8</sup> suggest that the reaction channels virtually all of its exoergicity into internal excitation of the OH. We shall return to this point in the next section, but first we consider the energy distribution created by the electronic-to-vibrational energy transfer, reaction (2).

The HCl vibrational distributions created in reaction (2) are shown in Fig. 3 for the same values of  $\langle Z_{GK} \rangle$  at which the OH data were taken. The absolute total cross section for this process, although less than one-tenth that of the reactive channel, is still quite large, especially in view of the fact that reaction (2) is a spin-forbidden process. The data for  $\langle Z_{GK} \rangle = 4$  show that the initial HCl vibrational distribution from this process is also strongly inverted. Although all of the vibrational levels ( $v' \leq 5$ ) are available, the interaction channels energy almost exclusively into HCl(v' = 4). This specificity suggests that the range of possible interactions, which can lead to energy transfer must be very restricted. The qualitative description of this interaction which best fits all these data is a collision on a singlet potential surface, forming an intermediate which does not form OH + Cl in a direct process, but lives long enough to find the region of intersection with the triplet surface. Since the spin change is not a highly probable process, the system likely remains in this region a long time before making the transition to the triplet surface.

The specificity indicated by the strongly peaked HCl vibrational distribution suggests that the products must all

$$O(^{1}D_{v}) + HCl \rightarrow HCl(v') + O$$



FIG. 3. The time evolution of the HCl vibrational distributions created in the E-V energy transfer process, reaction (2), recorded at the same times as the OH distributions shown in Fig. 2.

enter the triplet surface's exit channel in approximately the same region of phase space, and hence that there is only a restricted region of phase space where the transition from the singlet surface can occur. This is consistent with the expectation that the transition has a low probability. The specificity indicated by the peaked OH distribution, however, may arise from either of two causes. It may be simply due to a direct process in which OH and Cl are formed via a  ${}^{1}A$ " surface on which the reagents and products correlate directly, this process would have simple abstraction dynamics in which the  $O(^{1}D)$  atom removes one H atom without significant interaction with the other, or it could be the result of a more complicated process, still on a singlet surface such as the one which correlates with HOCl  $(\tilde{X}^{1}A')$ . In the latter case the vibrational specificity would have to be the result of specific dissociation dynamics, as suggested previously for the E-V channel, reaction (2). We shall return to this point in the next section, but first we consider the vibrational energy-transfer processes implied by the time dependences of the vibrational distributions shown in Figs. 2 and 3.

The vibrational distributions in both figures have been normalized such that  $\sum_{v'} P(v') = 1.0$  for each time delay. Although not strictly necessary, since the relative amplitudes of these signals are available from the measurement, this procedure makes the time dependence of the overall distribution clearer, and removes the effect of the bulk loss, with time, of emitters from the observation zone, which reduces the populations of all vibrational levels proportionately. The vast majority of the collision partners causing the vibrational relaxation of both products are the unused reagents, which are in at least a thousand-fold excess over the excited product molecules. Thus, as discussed earlier, it may be assumed that the relaxation of the OH, shown in Fig. 2, is caused by collisions with O<sub>3</sub> and HCl, both in their lowest vibrational states, and both present in approximately equal concentration. That both of these species are relatively efficient vibrational deactivators, is indicated by the rapid decrease in the relative populations of the OH (v = 4) levels, and the equally rapid increase in the lower levels. This deactivation pattern can be reproduced by assuming reasonable rate constants and integrating the appropriate rate equations, and it is the expected behavior for such a system. The vibrational dependences of the rate constants for relaxation of OH (v') by both O<sub>3</sub> and HCl will be obtained in future work on this system, by varying the concentrations of these reagents. The time dependence of the HCl vibrational distribution shown in Fig. 3 is more complicated than that of the OH. In fact, two (major) processes are occurring in this case. One is the deactivation of the higher levels in collisions with  $O_3$  and HCl; this is responsible for the decay of the v' = 3 and 4 levels and the (relative) increase in the v' = 3population. The other is the (much more rapid) increase in the HCl (v' = 1 and 2) levels due to the V–V processes:

$$OH(v) + HCl(0) \rightarrow OH(v - n) + HCl(m).$$
(7)

These processes are all exothermic for the case where  $m \leq n$ , and the most probable event, of course, is m = n. Since this process creates one vibrationally excited HCl for each OH deactivation, and since there is approximately 20 times more OH(v') produced in the reaction than HCl(v'), the initial rate of increase of  $HCl(v' \leq 2)$  is greater than the rate of decrease of the levels  $HCl(v' \ge 4)$ . The normalization of the distributions (separately) hides the fact that the total HCl(v) population increases with time and thus reduces the apparent rate of increase of the lower levels and increases the apparent rate of decrease of the upper levels. The future energy transfer work, mentioned previously, will also treat this V-V problem. This analysis was not carried out on the existing data because a better signal-to-noise ratio on the timedependent results is desirable and more experiments with different reagent concentrations are necessary to permit extraction of accurate (relative) rate constants. The present results will be used only to extract information about the initial vibrational distributions created by reactions (1) and (2).

#### **IV. DISCUSSION**

The reagents must approach on a singlet surface. At relative kinetic energies below about 2 eV, they correlate with three singlet states of HOCl: the  $\tilde{X}^{1}A'$  state and two higher states, one a  ${}^{1}A$ ", the other a  ${}^{1}A$ '. Only the lowest of these is energetically available to the HClO configuration, but the facility with which the H atom can react to forces released during the collision makes it unnecessary to distinguish between HClO and HOCl in the entrance channel. Those collisions which subsequently form the triplet products,  $O({}^{3}P) + HCl({}^{1}\Sigma_{e}^{+})$ , must undergo a spin reorientation and transfer onto a triplet surface. In view of the fact that it is a (formally) forbidden process, a surprisingly large number of the collisions lead to this spin reorientation.

The initial vibrational distributions in the diatomic products of both the singlet and triplet channels, reactions (1) and (2), respectively, are nearly identical. The maximum populations occur in both cases at a diatomic vibrational energy of  $134 \pm 5$  kJ/mol and both distributions are sharply peaked at this value. The fact that the HCl distribution is strongly inverted seems inconsistent with the implication that the system must remain in relatively close contact for a long time in order to permit the spin reorientation to occur. Nevertheless all of these observations are consistent with the description of the dynamics which we shall present below. The correlations and energetically accessible levels relevant to this discussion are shown in Fig. 4. The energy levels of the excited states of HOCl are taken from the calculations of Peyerimhoff and Buenker.<sup>37,38</sup> The range of energies accessible to the reagents [mostly in the excess translational energy in the  $O(^{1}D_{2})$  atom remaining from the ozone photodissociation] is indicated by the shaded area. The initial vibrational populations of OH and HCl (the distributions measured for  $Z_{GK} = 4$ ) are shown by the bars plotted at the energies of the respective vibrational states. The channel producing  $H(^{2}S) + ClO(^{2}\Pi)$  is not shown, although it is excergic ( $\Delta H_0^0 = -25 \text{ kJ/mol}$ ) and rate measurements<sup>4</sup> indicate that about 24% of the reaction yields these products. They cannot be detected in our experiments, however; and no discussion of the reaction dynamics in this channel will be given.



FIG. 4. The energy level and correlation diagram for the  $O(^{1}D)/HCl$  system. The energies of the HOCl states are the values for the equilibrium geometry of the ground electronic state.

It is clear that the reagents must either approach on the  ${}^{1}A'$  surface, which correlates with ground state HOCl, or on the  ${}^{1}A''$  surface which gives the second excited state of HOCl. In the former case, the strongly attractive HOCl minimum would make it unlikely that the system would return to the entrance channel; the most likely outcome would be rapid dissociation to OH( ${}^{2}\Pi$ ) + Cl, in a process formally similar to the O( ${}^{1}D_{2}$ )/H<sub>2</sub> reaction, which has been extensively discussed in the literature.<sup>10-20</sup>

Approach on the  ${}^{1}A$  " surface presents the only reasonable possibility of reaching the triplet products, because this surface comes very close in energy to the  ${}^{3}A'$  excited-state surface for large regions of configuration space. Figure 4 has been drawn for the equilibrium configuration of HOCl, for which the energies of the  $({}^{1}A")$  and  $({}^{3}A')$  surfaces differ by only about 18 kJ/mol, approximately the uncertainty in the calculation.<sup>37,38</sup> On moving the H atom towards more-linear configurations, the energy of the  ${}^{3}A'$  state decreases, and that of the  ${}^{1}A$  " state increases (slowly) so the energies become exactly degenerate for slightly larger HCLO angles.<sup>38</sup> These states also remain very close in energy as both the H-ClO and the HO-Cl bond lengths change. Their energies differ by only a few kJ/mol over the range of O-Cl bond distances out to 5 a.u. and for an H-OCl range from about 1.3 to 2.4 a.u.<sup>38</sup> There are also crossings in the HClO configuration, which behave similarly. The energetic degeneracy of these states over such a large region of configuration space enhances the probability of the spin-reorientation process, and is ultimately responsible for the presence of the  $O({}^{3}P) + HCl({}^{1}\Sigma_{o}^{+})$ products.

The near identity of the OH and HCl vibrational distributions is a coincidence too unusual to be caused by chance. There are several other similarities in this system which are also worth noting, as these reinforce the similarities in the dynamics implied by the remarkable resemblance of the diatomic product vibrational energy distributions. Both the reduced mass and the mass combination in the product channels (H + LH) are the same. Furthermore, the total energy released in both product channels is nearly identical. These similarities together with the similarity in overall behavior of the singlet and triplet potential energy surfaces (vide supra) strongly suggest a self-consistent interpretation of the overall dynamics of the  $O({}^{1}D_{2}) + HCl({}^{1}\Sigma_{g}^{+})$  interaction, which may be summarized as follows. The initial reagent approach along the  ${}^{1}A$  " surface proceeds rapidly, until the region of phase space near the  ${}^{3}A'$  surface is encountered. The kinematics of the collision are dominated by the motions of the two heavy atoms; the rapid motion of the H atom permits it to respond quickly to variations in the potential caused by the slower O-Cl encounter. This provides a mechanism for trapping the system in the region where the singlet and triplet surfaces are close in energy, because it is metastable for all  ${}^{1}A$  " configurations with small Cl-O distances. There are substantial barriers to the removal of the H atom for all bond angles of the triatomic in this region of configuration space. The potential minima in these configurations are nearly isoenergetic with the reagents, hence the small amount of energy released in the approach coordinate will be taken up by relatively slow Cl-O vibration while the rapid motion of the H atom permits the system to sample the singlet-triplet intersections many times during the Cl-O collision. The system is thereby trapped in a state which is nearly isoenergetic with the reagents for all configurations having small Cl-O separations. During this time, some of the systems transfer to the triplet surface. For the more collinear HOCl configurations, there is strong O-Cl repulsion in the  ${}^{1}A$ " state, leading to the dissociation channel which forms  $OH(^{2}\Pi) + Cl(^{2}P)$ . During the O-Cl separation which results from this repulsion, however, the  ${}^{3}A'$  state remains very close in energy, becoming exactly degenerate for Cl-OH separations around 3.5 a.u.<sup>38</sup> It is to be expected, therefore, that more systems will transfer to the triplet curve during the product separation. Again in this case, the rapid motion of the H atom will facilitate the nuclear reorganization necessary to permit separation to the other products,  $O(^{3}P) + HCl.$ 

It is clear from the preceding discussion that both sets of observed products originate from the same region of phase space, the (large) region for which the  ${}^{1}A$  " and  ${}^{3}A$  ' surfaces are close in energy. This, together with the identity of the exit channel mass combinations and energy release, suggests that the energy disposal into vibration of the two diatomic products should also be the same, as observed. The strong vibrational inversion in both diatomics indicate that they were formed from configurations in which the bond with the hydrogen atom is very long. This is consistent with a dynamical description in which the decomposition due to strong O–Cl repulsion occurs without regard to the H location and possibly involves transfer of the H between the two heavier atoms

at large internuclear separations of the latter in the exit channel. It is also consistent with earlier work<sup>5</sup> in which reaction between vibrationally excited OH and  $Cl(^{2}P)$  atoms was seen to produce vibrationally excited HCl and  $O(^{3}P)$  atoms, that is, the vibrational excitation of the OH reagent was carried over into vibrational excitation of the HCl product. All of the dynamical and energetic considerations presented so far in this section would suggest such a result.

In the discussion so far, we have omitted consideration of the  ${}^{1}A$  ' channel which correlates with ground state HOCl. Here, there is no nearly degenerate triplet state in the product channel and only one triplet intersection occurs for a small region of configuration space in the entrance channel. We expect, therefore, that reaction on this surface will lead predominantly to  $OH(^{2}\Pi) + Cl(^{2}P)$ . It is unlikely, although not impossible, that the reaction dynamics in this case would be the same as those of the systems which remain on the  ${}^{1}A$  " surface, and therefore, it is unclear why the total range of vibrational states populated by both reaction channels is so small. Either the overall dynamics are, in fact, very similar, dominated by the heavy atom collision, with the ultimate H-atom disposal being determined in the exit channel, or this interaction creates only OH(v'=0), which could not be detected by our experiment. The latter seems improbable in view of the large energy release and relatively weak binding in the HOCl( $\tilde{X}^{1}A'$ ) state, but it cannot be ruled out on the basis of the data recorded in this experiment.

#### **V. CONCLUSION**

We have observed the vibrational distributions in both the OH( $^{2}\Pi$ ) produced by reaction (1) and the HCl( $^{1}\Sigma_{e}^{+}$ ) created in reaction (2). The distributions in vibrational energy are nearly identical; both are strongly inverted. The ratio of reactions forming OH to those forming HCl is approximately 20:1, as observed in a previous rate measurement.<sup>4</sup> It is likely that both the OH and the HCl products come from the same part of the system's phase space, that region where the  ${}^{3}A'$  and  ${}^{1}A''$  states of electronically excited HOCl are close in energy. Microscopic reversibility, applied to both channels of this process, would indicate that the reaction between vibrationally excited  $OH(^{2}\Pi)$  and  $Cl(^{2}P)$  atoms would create vibrationally excited HCl and  $O({}^{3}P)$  atoms, a result which had already been observed in previous work on this system.<sup>5</sup> The dynamics of this reaction are dominated by the relatively slow O-Cl collision, together with the rapid H atom response to the changes in the potential generated by the motion of the heavy atoms. This permits the system to sample the singlet-triplet intersection regions many times during a single O-Cl collision, thus enhancing the probability for the nonadiabatic process, without requiring the formation of a long lived HOCl intermediate. Decomposition in the electronically excited channel is dominated by O-Cl repulsive energy release. The final disposal of the H atom is not important to this process, and occurs at large separations between the H and the heavy atom to which it is ultimately bonded. Reaction on the lowest  ${}^{1}A$  ' surface, which correlates with HOCl( $\widetilde{X}$ ), either has the same dynamics as the reaction on the electronically excited surface or creates OH(v'=0)exclusively, a result which we consider unlikely.

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