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# The state-to-state predissociation dynamics of OC–HF upon HF stretch excitation

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Photofragment angular and state distributions have been measured following the vibrational predissociation of the OC–HF complex. An F-center laser is used to pump the fundamental H–F stretching vibration of the complex and a second F-center laser is used to probe the rotational states of the HF fragment as a function of recoil angle. The complex dissociates via two different sets of channels, one that produces  $v_{\rm CO}=1$ ,  $J_{\rm HF}=6,5,4$  (intermolecular V-V transfer) and the other  $v_{\rm CO}=0$ ,  $J_{\rm HF}=11$  (V-R transfer). Analysis of the data gives correlated final state distributions, as well as an accurate value for the dissociation energy ( $D_0$ ) of the complex, namely 732±2 cm<sup>-1</sup>. © 2000 American Institute of Physics. [S0021-9606(00)00235-X]

### INTRODUCTION

Considerable progress has recently been made in both the spectroscopic and dynamical characterization of weakly bound complexes. The nonstatistical nature of the vibrational dynamics of these complexes is of particular interest since the preferences these systems show for dissociating in specific ways provide insights into the nature of the interactions that lead to rupture of the weak bond. For very weakly interacting systems, such as Ar-HCl (Ref. 1) and Ar-HF,<sup>2,3</sup> the spectroscopic characterization can be quite complete, providing unique determinations of the corresponding intermolecular potentials.<sup>4–8</sup> At the other extreme are the hydrogen bonded complexes, including the HF dimer<sup>9,10</sup> and HCN-HF,<sup>11</sup> where even the extensive experimental studies that have been reported are insufficient to completely determine the potential energy surface. In these cases, ab initio calculations are often used to interpolate between the regions that are probed by the experiments. The linear  $N_2$ -HF (Refs. 12-15) and OC-HF (Refs. 16-21) complexes fall between these two limits, being characterized as having weak hydrogen bonds. Although there have been a large number of detailed experimental<sup>12-21</sup> and theoretical studies<sup>15,22-34</sup> of these complexes, a quantitative interaction potential is not available for either.

In the present study we use the optothermal detection method in combination with two F-center lasers to study the vibrational predissociation of the OC–HF complex. The first studies of this complex were carried out using microwave spectroscopy,<sup>16,17</sup> which revealed it to have a linear structure. More recent infrared studies have provided detailed information on a number of intramolecular vibrational modes of the complex,<sup>18–21</sup> as well as some insights into the nature of the associated vibrational dynamics. One of the interesting aspects of the latter came from our studies of the H–F stretch fundamental, which showed a very interesting perturbation that could only be explained in terms of a (dark) state that has more energy in the intermolecular degrees of freedom than the dissociation energy of the complex.<sup>19</sup> Despite this, the vibrational predissociation lifetime of this state has to be longer than that of the H–F fundamental to explain the experimental results. The implication seemed to be that there is very weak coupling between the corresponding bending (or internal rotation) degrees of freedom and the dissociation coordinate, namely the intermolecular stretching mode, such that the complex can store energy in the intermolecular modes (in excess of the bond energy) for a significant period of time.

The OC–HF complex has also been the subject of considerable theoretical work, including several that provide predictions of the intermolecular bond dissociation energy.<sup>24,25,27–32,34</sup> The present state-to-state experiments provide further insights into the nature of the energy transfer processes that lead to dissociation and an accurate value for the dissociation energy of the complex.

#### EXPERIMENT

The experimental approach used in this experiment involves measuring the photofragment angular distribution resulting from vibrational predissociation of the OC-HF complex, following excitation of the H-F stretching vibration. The translational energy release for a given final state channel, which determines the laboratory recoil angle, is anticorrelated with the total internal energy of the fragments. As a result, data of this type can provide detailed information on the final state distributions of the fragments, including the interfragment correlations. In particular, one can determine not only the state distribution of the HF fragment, but also which of these states correlate with specific states of the CO fragment, for a given dissociation event. To achieve this level of characterization, it is necessary to assign all of the structure observed in the angular distribution to specific internal photofragment states.

The molecular beam apparatus has been discussed in detail elsewhere.<sup>35,36</sup> In short, an F-center laser is used to excite the H–F stretching vibration of OC–HF and the resulting photofragments are detected using a bolometer detector.<sup>37</sup> The source can be rotated so that a complete photofragment angular distribution can be measured for a given initial state

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to TP: 131.230.73.202 On: Mon. 22 Dec 2014 15:21:46 of the complex. The F-center laser is equipped with an evacuated chamber containing three confocal etalons with free spectral ranges of 7.5 GHz, 750 MHz, and 150 MHz. These are used in combination with a wavemeter to monitor the tuning of the lasers. To obtain a full angular distribution, the pump laser must be kept in resonance with an OC-HF transition for approximately 45 min. This presented no serious problems in this case owing to the fact that the corresponding transitions were quite broad.<sup>19</sup> Angular distributions for the particular initial state of the complex were recorded by varying the angle between the molecular beam and the line joining the photolysis volume to the detector in 0.25° increments. The detailed kinematics that relate these angular distributions to the associated kinetic energy release for a given dissociation channel have been discussed elsewhere.35,38

A second F-center laser is used to probe the internal states of the HF fragment. In this case, the bolometer detects the extra vibrational energy deposited in the HF fragment by the probe laser. In the present study, we amplitude modulated the pump laser, which was fixed at the OC–HF transition frequency, and scanned the cw probe laser through the HF monomer transitions of interest. This modulation scheme has the advantage that probe laser signals are entirely due to HF monomer that is produced by the photolysis laser. One disadvantage is that the probe laser signal. Fortunately these background signals were quite stable and an average of 25 probe laser scans gave reliable results at each laboratory angle.

As discussed in detail previously,<sup>39–43</sup> extensive use has been made in our laboratory of the pendular state orientation method to enhance the information content in these experimental angular distributions. This involves orienting the parent molecule in the laboratory frame, such that the two fragments (in this case CO and HF) recoil in opposite directions in the laboratory frame and can be detected separately. Orientation of the parent complex is achieved by applying a moderate dc electric field (19 kV/cm) to the photolysis region and taking advantage of the fact that the dipole moment of the OC–HF complex will be oriented in the direction of the electric field. Since the bolometer is an energy detector, the relative signal levels depend upon the energy content of the two fragments. This information is extremely helpful in determining the internal states of the two cofragments.

In the present study the molecular beam was formed by expanding a mixture of 0.6% HF and 30% CO in helium through a 40  $\mu$ m diam nozzle, from a source pressure of 550 kPa. In order to relate the recoil angle of a fragment to the associated recoil energy, an accurate measurement of the stream velocity of the molecular beam is needed. This was accomplished by Doppler spectroscopy, yielding a stream velocity of 1300 m/s for the present expansion conditions.

#### RESULTS

In all of the experiments reported here the laser polarization was aligned parallel to the dc field, such that the relevant selection rule is  $\Delta M = 0.39$  Under these conditions, the electric field induced transitions of a linear molecule ap-



FIG. 1. A pendular state spectrum of the OC–HF complex, recorded at a field strength of 19 kV/cm. Note that the field was switched off while scanning the high frequency portion of the spectrum in order to record the field free R(0) transition. The vertical arrow at  $v_0$  indicates the position of the field free vibrational origin of the complex. The solid line through the pendular spectrum was calculated based upon the molecular constants obtained previously for this complex (Ref. 19). The inset shows the orientation distribution for the complex at this applied field.

pear near the vibrational band origin of the spectrum, as shown in Fig. 1. This spectrum was recorded by first scanning through the R(0) transition with the dc field off (providing an absolute frequency calibration) and then turning the field on to record the pendular spectrum. The fieldinduced transitions are spaced by an amount that depends on the difference in the rotational constant and dipole moment between the vibrational ground and vibrational excited states. The smooth solid line through the data is a calculation based upon the molecular constants for OC-HF reported elsewhere.<sup>19</sup> The good agreement ensures that we have properly assigned the corresponding states and that the orientation distribution used to analyze the photodissociation experiments is correct. The inset in the figure shows the orientation distribution at the electric field corresponding to the one used in the spectrum, namely, 19 kV/cm.

We began the photodissociation studies by recording an angular distribution in the absence of the electric field, corresponding to the R(0) transition shown in Fig. 1. This transition provides the best resolution in the photofragment distributions (assuming that dissociation occurs via axial recoil) when the laser polarization is aligned perpendicular to the molecular beam axis.<sup>38</sup> In this case, the excited state alignment imposed by the excitation laser ensures that the most probable recoil direction in the laboratory frame is orthogonal to the molecular beam, giving rise to the maximum possible laboratory frame recoil angle for a given translational energy release. As a result, the fragment channels with different translational energies scatter to quite different laboratory angles. In contrast, if the laser polarization is aligned parallel to the molecular beam direction, the photofragments are preferentially ejected along the beam and the various final state channels all scatter near zero degrees in the labo-



FIG. 2. An angular distribution obtained by pumping the R(0) transition of the OC–HF complex, with the laser polarization direction aligned perpendicular to the molecular beam axis. The dashed line through the data is a calculation based upon the probabilities determined from the pendular state results. The good agreement indicates that the applied electric field used to obtain the oriented angular distributions has little or no influence on the photodissociation dynamics of this system.

ratory frame. A detailed discussion of these zero electric field cases, in relation to the photodissociation of the HF dimer, can be found elsewhere.<sup>38</sup>

The angular distribution obtained by pumping the R(0) transition is shown in Fig. 2. From a first inspection of the data it becomes clear that there are a number of important final state channels having different recoil energies. This is fortunate since our goal here is to assign the individual peaks in the angular distribution to specific final state channels and the more structure that is present in the angular distributions, the better our chances of making a unique assignment. There are several problems that must be addressed if we are to explain the structure observed in this angular distribution. The first is simply to choose from the many open channels, the few that contribute to the distribution. Figure 3 shows an energy level diagram that illustrates the difficulty here. There



FIG. 3. An energy level diagram for the OC–HF system. The horizontal dashed line indicates the available energy (3112 cm<sup>-1</sup>), based upon the laser excitation energy (3844 cm<sup>-1</sup>) minus the dissociation energy (732 cm<sup>-1</sup>) determined from the experimental results. All open rotational states of the HF fragment are depicted, upon which are built the CO rotational levels. Two main sets of channels can be identified corresponding to  $v_{\rm CO}=0$  and  $v_{\rm CO}=1$ . HF rotational states observed in the present study are indicated (\*).



FIG. 4. A set of pendular state angular distributions, corresponding to excitation of the most intense pendular transition in Fig. 1. This transition pumps the M=0 excited state, which is the most highly oriented by the electric field. The HF and CO fragments appear at positive and negative angles, respectively. The solid line through the data points is the result of a fit to the data, as described in the text.

are clearly many open channels, so many in fact that if all were populated statistically, we would not observe the distinct peaks evident in Fig. 2. From this we can immediately conclude that the dissociation is nonstatistical for this system, a situation that is generally encountered in the dissociation of these weakly bound systems. The second problem is that we do not have an accurate value for the dissociation energy of this complex, so that the location of the horizontal line in Fig. 3, which represents the available energy upon excitation of the H-F stretch, is not known. The final problem is that the bolometer used to measure the angular distribution is sensitive to both the CO and HF fragments. Thus the angular distribution shown in Fig. 2 has contributions from two fragments of different masses. Since conservation of momentum tells us that these two fragments have different recoil velocities, this angular distribution is really the superposition of two distributions. Thus each final state channel will give rise to two peaks in the angular distribution, making its assignment even more difficult. In what follows we will address these problems in turn.

We begin with the problem of separating the angular distributions associated with the CO and HF fragments. As indicated above, this can be done using the pendular state orientation method. As shown by the inset in Fig. 1, the OC-HF complex is oriented by the strong field, such that the HF and CO fragments recoil in opposite directions, towards the positive and negative electrodes, respectively. As a result, angular distributions recorded on the positive and negative electrode sides of the apparatus, while pumping the most intense pendular state transition in Fig. 1, will correspond to the HF and CO fragments, respectively. Figure 4 shows a set of angular distributions obtained in this way. The structure in the angular distributions is now better resolved and each peak must be due to a different photofragment channel. It is interesting to note that the relative intensities of the two main peaks observed on either side are different, the preliminary indication that they come from channels with very different partitioning of the available energy between the two frag-

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FIG. 5. A comparison between the HF angular distribution and that obtained by probing the HF P(11) transition. A typical probe laser scan through this transition is shown as an inset. The dashed line through the probe data shows the  $v_{CO}=0$ ,  $J_{HF}=11$  contribution to the fit in Fig. 4.

ments. The fact that the peak at smaller angles is relatively larger on the CO side of the distribution, suggests that the corresponding photofragment channel has a significant fraction of the available energy in the CO fragment. This will be confirmed in what follows. The fact that we do not known the dissociation energy of this complex still makes the assignment of these peaks to specific final state channels somewhat challenging. Indeed, by varying the dissociation energy we can bring any number of channels to the correct energy to account for the peaks in the angular distribution.

The next step is to use the second, probe laser to measure angular distributions corresponding to individual HF rotational states. It is important to note that only the v = 0 state of the HF fragment is energetically accessible in these experiments. To perform such a pump-probe experiment, we first positioned the apparatus near an intensity maximum of the HF fragment distribution and searched for signals associated with the various HF rotational transitions [R(0), P(1)]through P(13)]. At 10° we found that only the transitions originating from the  $J_{\rm HF}$ =11 and  $J_{\rm HF}$ =6 states of HF had significant intensity. We should note here that the P(5) transition was inaccessible due to the fact that it overlaps a strong water vapor transition. The present result is quite similar to that observed for N<sub>2</sub>-HF, where only the  $J_{\rm HF}$ =12 and  $J_{\rm HF}$ =7 states were populated, corresponding to production of the N2 fragment in the ground and vibrationally excited states, respectively.<sup>40</sup>

Figure 5 shows a comparison between the total HF angular distribution obtained from the pendular state excitation and that obtained by probing only the  $J_{\rm HF}$ =11 state. The inset in the figure shows a typical probe spectrum corresponding to the P(11) transition. Although the signal to noise ratio of the state specific angular distribution is rather poor, it clearly shows that most of the signal at larger angles comes from the  $J_{\rm HF}$ =11 channel. The most prominent difference between the total angular distribution and that corresponding to  $J_{\rm HF}$ =11 is that the latter does not show the pronounced peak near 10°, suggesting that the  $J_{\rm HF}$ =6 state



FIG. 6. A comparison between the HF angular distribution and that obtained by probing the HF P(6) transition. A typical probe laser scan through this transition is shown as an inset. The dashed line through the probe data corresponds to the  $v_{\rm CO}$ =1,  $J_{\rm HF}$ =6 contribution to the fit in Fig. 4.

contributes most significantly in this region. To test this, we recorded a state specific angular distribution for  $J_{\rm HF}=6$ , which is shown in Fig. 6. Once again, the inset shows a typical probe laser scan of the P(6) transition. Note that the relative intensities of the state specific angular distributions in Figs. 5 and 6 have been scaled so that their sum gives the best fit to the overall distribution, which is in qualitative agreement with the relative transition intensities. It is clear from Fig. 6 that the  $J_{\rm HF}$  = 6 state only contributes at smaller angles and peaks in the correct place to account for the differences between the two distributions in Fig. 5. The fact that the  $J_{\rm HF}$  = 6 channel appears at smaller angles than  $J_{\rm HF}$  = 11 can be appreciated from the energy level diagram in Fig. 3. Given the available energy, the  $J_{\rm HF}$  = 11 channel can only be produced in coincidence with the  $v_{\rm CO}=0$  state. On the other hand, if  $J_{\rm HF}$  = 6 where produced in coincidence with  $v_{\rm CO}$ =0 and the fragments were detected at 10°, the CO fragment would have to carry away approximately two thousand wave numbers of rotational energy. Given the small rotational constant for CO [1.9225 cm<sup>-1</sup> (Ref. 44)], this would necessitate populating the  $J_{CO}=39$  state. Such a large change in rotational quantum number upon dissociation seems unlikely and we have never seen such in the systems we have studied. As a result, we conclude that the  $J_{\rm HF}$  = 6 channel is produced in coincidence with the  $v_{\rm CO}=1$  state. As Fig. 3 illustrates, this places the two channels at just the right relative energies to explain the experimental data. Clearly the internal energy of the  $J_{\rm HF}$  = 6,  $v_{\rm CO}$  = 1 channel is larger than that of the  $J_{\rm HF}$ =11,  $v_{\rm CO}$ =0 channel, explaining why the latter scatters to larger angles.

The sharp cut off of the  $J_{\rm HF}$ = 6 channel is helpful in that it provides an accurate determination of the dissociation energy of the complex. The highest recoil energy occurs when the CO is produced in the  $J_{\rm CO}$ =0 state. The best overall fit to the data was obtained with a dissociation energy of 732 cm<sup>-1</sup>, which is the value used in Fig. 3. The solid line through the experimental data in Fig. 4 is the result of a least squares fit that uses a Monte Carlo procedure to include the instrumental factors that control the resolution of the apparatus. The only fitting parameters were the individual probabilities for the various open channels. The dashed lines through the state specific angular distributions in Figs. 5 and 6 are the contributions from the corresponding states, obtained from the fit. This excellent fit to all of the data could only be obtained for a dissociation energy of  $732\pm2$  cm<sup>-1</sup>, making the assignment unique.

It is important to point out that the relative intensities on the CO and HF sides of the angular distribution provide further confirmation that we have properly assigned the final state channels. Indeed, other combinations were tried but did not give the correct relative intensity. This is due to the fact that the bolometer is an energy detector, so that the relative intensities depend upon which fragment carries away the larger fraction of the available energy. We should also point out that the final fit included contributions from the  $J_{\rm HF}$ =5,  $v_{\rm CO}=1$  and  $J_{\rm HF}=4$ ,  $v_{\rm CO}=1$  channels (even though we did not probe these) to account for some of the signals at larger angles. Fits that did not include these channels showed too much structure in the angular distribution at large angles and did not give the correct relative intensities for the CO and HF angular distributions. Therefore, although we do not have probe laser results for  $J_{\rm HF}$  = 4 and 5, the data strongly suggests that these are populated. Further support for this comes from the fact that the probe laser induced signals for the  $J_{\rm HF}$  = 11 state of HF (relative to the total signals) are smaller in this system than in others we have studied, where we were certain that only  $J_{\rm HF}$  = 11 contributed.<sup>45</sup> Indeed, experiments on OC-HF and acetylene-HF, carried out back-to-back, consistently gave probe laser signals for the former that were 25% smaller, relative to the total signal, than the corresponding signals for the latter. The implication is that in OC-HF (at larger angles) there are contributions to the total signal from states other than  $J_{\rm HF}$  = 11, in qualitative agreement with the results from the fit. From the fit shown in Fig. 4, a complete set of individual state-to-state probabilities was obtained for the various state channels and is available through EPAPS.<sup>46</sup> Nevertheless, some of these probabilities are interdependent. Therefore, the best way to make comparisons with theoretical calculations of the state-to-state probabilities is to calculate the full angular distribution. For the present purposes, we note that the probabilities obtained from these channels indicate that the V-V and V-R channels are equally probable to within the experimental uncertainty.

The state distribution obtained from fitting the experimental results is highly nonstatistical. This is further illustrated in Fig. 7, which shows a comparison between the experimental angular distributions and the results of a purely statistical calculation,<sup>47,48</sup> the latter shown as the solid line. In the past<sup>41,42,45,49</sup> we have found much better agreement with a restricted phase space calculation, in which the two high frequency modes of the system, namely, the HF rotation and the CO vibration in this case, were constrained to agree with the experimental results. In this case, only the rotation of the heavy fragment and the translational degrees of freedom are treated statistically. The dashed line in Fig. 7 shows the result of such a calculation. Although the overall width of the angular distribution is more faithfully reproduced in this



FIG. 7. Comparisons between the experimental angular distributions (data points) and those of a full statistical calculation (solid line) and a restricted phase space calculation (dashed line), as described in the text.

case, the agreement is still rather poor, due to the fact that the statistical calculation tends to overestimate the contributions from the higher CO rotational states.

It is important to consider whether or not the electric field, used to orient the complex, has any effect on the state-to-state dynamics. To test this, we used the state-to-state probabilities obtained from the pendular state angular distributions to calculate the angular distribution for the field free R(0) transition. The result is shown as the solid line in Fig. 2, which is in reasonably good agreement with experiment. This is in agreement with the previous systems we have studied<sup>42,45,50</sup> that also show that the electric field has no significant influence on the state-to-state dynamics.

Finally, we consider the states that showed interesting perturbations in the spectroscopy at zero electric field.<sup>19</sup> The pendular spectrum showed no evidence of perturbations so that studies of these had to be carried out at zero electric field. In view of the fact that the character of the perturbing state is known to be quite different from the H-F stretch fundamental, we might expect that the corresponding final state distributions would also be quite different. Thus experiments designed to probe these final states could provide further insights into the nature of the corresponding dark states. Angular distributions were recorded for the two components of the perturbed R(6) transition. However, within the experimental uncertainties the two angular distributions were the same. In retrospect, this is not unexpected, given that the perturbing state has a significantly longer predissociation lifetime than the H-F fundamental.<sup>19</sup> Thus, even though the final state distribution from the dark state is likely to be quite different from the bright state (the H-F stretch), the dissociation rate out of the former is too slow to contribute significantly to the experimental results.

## DISCUSSION

In the previous section we presented detailed results related to the state-to-state photodissociation dynamics of the

OC-HF complex, corresponding to excitation of the H-F stretch. Broadly speaking, dissociation proceeds via two distinctly different channels, namely a V-V channel, where most of the energy is transferred from the HF molecule to the CO fragment and a V-R channel, corresponding to the HF fragment carrying away most of the energy in rotation. The state-to-state probabilities can now be used to determine the partitioning of the available energy among the various degrees of freedom of the fragments. The total available energy to the fragments is simply the difference between the photon excitation energy (3844 cm<sup>-1</sup>) and the dissociation energy determined above  $(732 \text{ cm}^{-1})$ , namely,  $3112 \text{ cm}^{-1}$ . Consider first the V-R channel, for which the CO fragment is produced in the ground vibrational state, so that  $E_v^{\text{CO}} = 0$ . The energy of the  $J_{\text{HF}} = 11$  state is 2677 cm<sup>-1</sup>,<sup>51</sup> thus accounting for most of the available energy (86%). If we average over the rotational states of the CO fragment, the average translational energy release for this channel is  $E_t = 254 \text{ cm}^{-1}$  (8%), while  $E_R^{CO} = 181 \text{ cm}^{-1}$  (6%). Next, we consider the V - Vchannel, where the majority of the available energy now appears as vibration of the CO fragment, namely,  $E_n^{CO}$ =  $2143 \text{ cm}^{-1}$  (69%). In this case, the average energy in HF rotation is  $E_J^{\text{HF}} = 555 \text{ cm}^{-1}$  (18%), while  $E_J^{\text{CO}} = 97 \text{ cm}^{-1}$ (3%). The translational recoil energy, averaged over the  $J_{\rm HF} = 6,5,4$  states, is  $E_t = 317 \, {\rm cm}^{-1}$  (10%). In both of these channels, therefore, translation and heavy molecule rotation account for only a small fraction of the excess energy.

The dissociation energy  $(D_0)$  of the OC-HF complex has been determined in this study to be  $732\pm2$  cm<sup>-1</sup>. We can compare this value with previous estimates from both experiment<sup>16</sup> and theory.<sup>24,25,27–32,34</sup> The only previous experimental estimate of  $D_0$  was obtained by Legon *et al.*<sup>16</sup> by fitting the microwave results to a pseudodiatomic model, yielding 987 cm<sup>-1</sup>. This approach is well known to give unreliable results, so that the disagreement with the present results is not surprising. Many ab initio calculations have been carried out on the OC-HF complex,<sup>24,25,27-29,31,32,34</sup> as well as molecular modeling studies.<sup>30</sup> In the present discussion we focus only on the most recent results, which we assume are the most accurate. The main problem with making comparisons between experimental  $D_0$  values and those obtained from ab initio theory is that the latter suffer from two problems. The first is just the level of the calculations (basis sets, etc.) and the second is the estimate of the zero point energy, which is often done using harmonic frequencies. For example, Curtiss et al.<sup>28</sup> have reported calculations at the MP3 level, yielding  $D_e = 1172 \text{ cm}^{-1}$  and  $D_0$  $= 539 \,\mathrm{cm}^{-1}$ . This is to be compared with the most recent work of Handy and co-workers,<sup>31</sup> which yielded  $D_e$ =  $1199 \text{ cm}^{-1}$  and  $D_0 = 583 \text{ cm}^{-1}$ . In both cases, the zero point energy was estimated from the harmonic frequencies. Since the latter are larger than the anharmonic frequencies, we can assume that the zero point energy correction is too large and that the true  $D_0$  will be somewhat larger. Thus, although these calculated dissociation energies are expectedly smaller than the present experimental value, the comparisons are unsatisfactory at the quantitative level. Nevertheless, the results do suggest that the problem is mainly with the estimate of the zero point energy, suggesting that the *ab*  *initio* potential surface is probably much better than this lack of agreement would imply.

#### SUMMARY

In the previous sections we have presented data that gives a rather complete picture of the state-to-state photodissociation dynamics of the OC-HF complex, resulting from excitation of the H-F stretching vibration. The complex is observed to dissociate via two distinctly different channels, namely, a V-R process which produces the HF fragment in J=11 and an intermolecular V-V channel, for which vibrationally excited CO (v = 1) is produced in combination with the HF fragment in J=6, 5, and 4. This assignment of the final state channels is based upon simultaneous fits to the angular distributions of the HF and CO fragments and the direct measurements of the state-specific angular distributions for  $J_{\rm HF}$  = 11 and 6. The correlated final state distributions show that the vibrational predissociation of this complex is highly nonstatistical. What is surprising about these results is that two such different channels have similar rates. Indeed, the V-R channel relies on coupling provided by the anisotropy of the intermolecular potential in order to access the  $J_{\rm HF}$  = 11 state. On the other hand, the V-V channel results from a coupling between the stretching modes of the two diatomic molecules provided by the intermolecular interaction. The fact that these two are of comparable magnitude is surprising. What is even more interesting is the fact that the same is observed in N<sub>2</sub>-HF, where we again observe both channels.<sup>40</sup> Full 6D potentials, along with the corresponding dynamical calculations, are needed to provide us with further insights into the reason for this interesting coincidence. The dissociation energy of the complex is determined in the present study to be  $D_0 = 732 \pm 2 \text{ cm}^{-1}$ .

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