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## Infrared Multiphoton Dissociation of the Methanol Solvate of the Fluoride Ion, $CH_3OHF^-$

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**Abstract:** The infrared multiphoton dissociation of the methanol solvate of the fluoride ion,  $CH_3OHF^-$ , has been studied under collisionless conditions using pulsed ion cyclotron resonance spectroscopy in conjunction with a pulsed TEA  $CO_2$  laser. Photodissociation spectra and fluence dependences for both chemically activated and collisionally relaxed  $CH_3OHF^-$  as well as an estimate of the number of ion-molecule collisions required to relax the chemically activated ion are presented. The data suggest that 40-80 ion-molecule collisions are required to relax excess vibrational excitation in the ion and that a species which is estimated to be in the vibrational quasi-continuum can retain structured features in its infrared absorption spectrum.

The activation of gas phase ions via infrared (IR) multiphoton absorption can, as in the case of neutral molecules, result in collision-free photodissociation.<sup>1</sup> This technique provides a novel and useful method for studying the dynamics of unimolecular ion decomposition and permits the vibrational spectroscopy of ions to be investigated in the absence of solvent and counterions. We have recently demonstrated that the IR multiphoton dissociation of gas-phase ions can be useful in studying the collisional relaxation of internal energy in vibrationally excited ions,<sup>2,3</sup> and we have shown that the dependence of the IR photodissociation yield on laser fluence can serve as a probe of some important aspects of the photophysics of IR multiphoton absorption.<sup>1,4</sup> In the case of the ion  $CH_3OHF^-$ , our results showed<sup>4</sup> that structured absorption features are found in the rovibrational spectrum even when excess vibrational energy is present in the ion. This paper provides a detailed discussion of our studies of the IR photodissociation of  $CH_3OHF^-$ .

The photodissociation of gas-phase ions induced by single UV-visible photon absorption has been studied by using ion beam and trapped ion techniques.<sup>5</sup> Both methods provide information on the electronic spectroscopy of ions, assuming that the quantum yield for photodissociation is independent of irradiation wavelength. The use of lasers as the excitation source permits high-resolution spectroscopic data to be obtained from such experiments.<sup>6</sup> In cases where the dissociation threshold exceeds the energy of a single photon, dissociation due to two-photon absorption,<sup>7</sup> and more recently four-photon absorption,<sup>8</sup> has been observed. Two-photon activation occurs via a sequential absorption process proceeding through a long-lived intermediate state generated after one photon has been absorbed. Ion-molecule collisions are observed to reduce the photodissociation rate by quenching the intermediate.<sup>9</sup>

Beauchamp and co-workers have demonstrated that ion photodissociation can be induced by sequential IR multiphoton absorption of tens of photons when a continuous-wave  $CO_2$  laser is used as the excitation source.<sup>10-13</sup>

Most studies of IR multiphoton dissociation reported to date involve the irradiation of neutral molecules with the output of a pulsed TEA  $CO_2$  laser.<sup>14-16</sup> These studies are generally interpreted in terms of a model for molecular rovibrational level structure similar to that shown in Figure 1. At low energies (the discrete level regime) the number of photons absorbed by a molecule may be sensitive to irradiation wavelength and laser intensity. At sufficiently high internal energies, the spacing between rovibrational energy levels is less than or equal to the laser bandwidth. This condition is usually used to define the quasi-continuum.<sup>14a</sup> It has been suggested that absorption in this regime is not strongly dependent on the laser wavelength and that photon absorption in the quasi-continuum depends primarily on laser fluence (integrated intensity) but is independent of laser intensity.<sup>14b</sup> This model provides a useful starting point in characterizing some of the photophysical details of IR multiphoton absorption, but important questions remain beyond the scope of this simple scheme. For example, what role do rotational selection rules play in vibrational transitions in the discrete level regime and in the quasi-continuum? Do all rovibrational transitions in the quasi-continuum have equal oscillator strengths, or does the absorption

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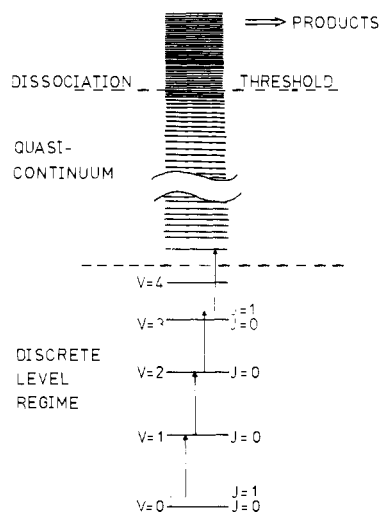


Figure 1. Schematic diagram of vibrational level structure associated with infrared multiphoton dissociation.

spectrum in this regime remain structured? Answers to questions of this nature are central to the development of a complete understanding of IR photoactivation.

We describe here studies of the IR multiphoton dissociation of  $\text{CH}_3\text{OH}^-$ . In our experiments, ions are generated, trapped, and detected by using a pulsed ion cyclotron resonance (ICR) spectrometer. At a selected time during the trapping period, ions are irradiated with light from a  $\text{CO}_2$  TEA laser, and the fractional decomposition due to photodissociation is determined. Because  $\text{CH}_3\text{OH}^-$  is formed via a rather exothermic ion-molecule reaction, a substantial amount of this energy may appear as vibrational excitation of the newly formed ion, which can then be relaxed by subsequent ion-molecule collisions. Thus, by varying the time at which  $\text{CH}_3\text{OH}^-$  is photolyzed after its formation, we find that we can study the photodissociation of either chemically activated or collisionally relaxed ions. We find that the collisional relaxation of  $\text{CH}_3\text{OH}^-$  requires approximately 40–80 ion-molecule collisions. The IR photodissociation spectrum of both chemically activated and collisionally relaxed  $\text{CH}_3\text{OH}^-$  has been measured. Additionally, the dependence of the photodissociation yield on laser fluence is examined for activated and relaxed ions. These data indicate that only a fraction of the  $\text{CH}_3\text{OH}^-$  population undergoes efficient photodissociation and that the size of this fraction depends on the irradiation wavelength in the case of activated ions. This implies that the chemically activated ions, which are estimated to be in the quasi-continuum, have a structured absorption spectrum. Our results suggest that IR multiphoton dissociation studies of gas-phase ions can provide important information on the spectroscopy and vibrational relaxation of gas-phase ions as well as important information on the photophysics of IR multiphoton processes.

### Experimental Section

A complete description of the pulsed ICR and TEA  $\text{CO}_2$  laser used in our work as well as details of the experimental technique appear elsewhere.<sup>1</sup> The pulsed ICR is of standard design<sup>17</sup> but employs a trapped ion analyzer cell specially designed and constructed for IR multiphoton experiments.<sup>1</sup> The laser is a Lumonics TEA-103-2  $\text{CO}_2$  laser operated multimode at a pulse repetition rate of 0.8  $\text{s}^{-1}$ . This apparatus allows us to measure the total photodissociation yield following a single laser pulse under conditions such that there are no ion-molecule collisions during the laser pulse nor for a minimum of several milliseconds after the laser pulse.

Thermal electrons were continuously ejected from the ICR cell by using trapping plate ejection.<sup>18</sup> When photodissociation yields were measured the  $\text{CH}_3\text{OH}^-$  signal was monitored 100 ms after the laser pulse and the photoproduct  $\text{F}^-$  was ejected by using the ICR double-resonance technique<sup>19</sup> during and after the laser pulse. Typical ICR

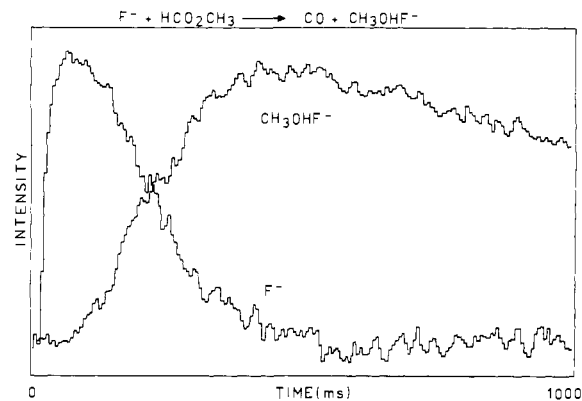


Figure 2.  $\text{F}^-$  and  $\text{CH}_3\text{OH}^-$  signal intensities vs. time due to reaction 4.

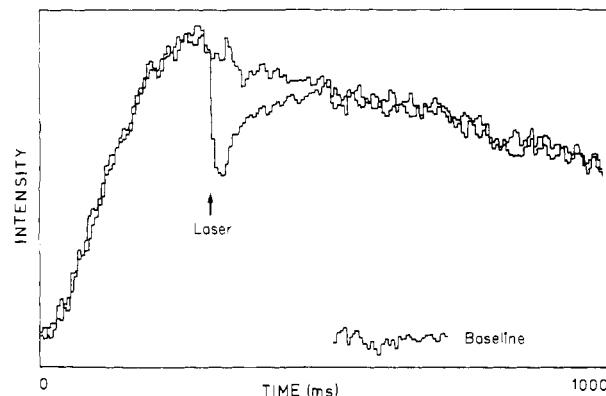


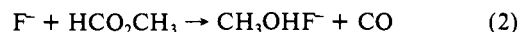
Figure 3.  $\text{CH}_3\text{OH}^-$  signal intensity vs. time with and without laser irradiation. No double-resonance ejection of  $\text{F}^-$  is employed. Compare to Figure 4.

operating conditions included a trapping voltage of 2 V and a marginal oscillator frequency of 307 kHz. Fluence dependences were obtained by attenuating the fixed-length laser pulse with polyethylene sheets and/or  $\text{CaF}_2$  flats. Primary negative ions were generated via dissociative electron capture using 1–2-eV electrons.

Nitrogen trifluoride, methyl formate, and 1,1,1-trifluoroethane were obtained from commercial sources and were used without further purification. Dimethyl peroxide was prepared by the method of Hanst and Calvert.<sup>20</sup> All compounds were degassed by several freeze-pump-thaw cycles on the ICR foreline prior to use. Pressures were measured in the  $10^{-8}$ – $10^{-5}$  torr range by using a Varian UHV-24 ionization gauge which was calibrated in the  $10^{-5}$  torr range for each neutral gas with an MKS Baratron capacitance manometer.

### Results

The methanol solvate of the fluoride ion,  $\text{CH}_3\text{OH}^-$ , was generated<sup>21</sup> by the reaction sequence shown in reactions 1 and 2. Time dependences for the decay of the  $\text{F}^-$  signal and the rise



of the  $\text{CH}_3\text{OH}^-$  signal are shown in Figure 2. From the pseudo-first-order behavior of these signals and the pressure of methyl formate, we find the rate constant for eq 2 to be  $(9.4 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Irradiation of the  $\text{CH}_3\text{OH}^-$  ion with the output from our pulsed  $\text{CO}_2$  laser results in photodissociation via reaction 3. The endothermicity of reaction 3 is



reported<sup>22</sup> to be 24  $\text{kcal mol}^{-1}$  so  $\text{CH}_3\text{OH}^-$  must absorb about nine  $\text{CO}_2$  laser photons to dissociate, assuming the ions are

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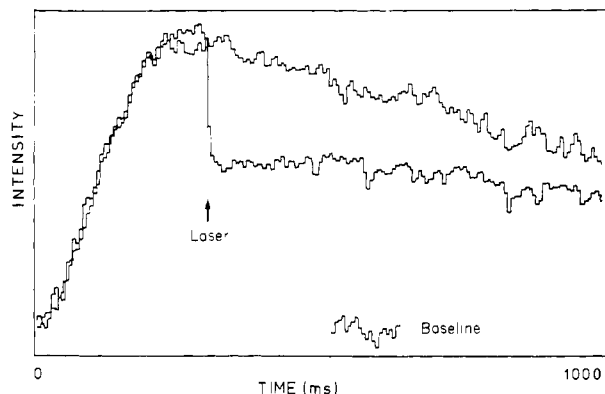


Figure 4. Intensity vs. time curves for the ion  $\text{CH}_3\text{OHF}^-$  with and without laser irradiation.  $\text{F}^-$  ejected with double resonance.

thermalized at 300 K prior to irradiation. The data in Figures 3 and 4 demonstrate that reaction 3 is the only observed photodissociation pathway. Figure 3 shows the time dependence of the  $\text{CH}_3\text{OHF}^-$  signal in the presence and absence of irradiation. Coincident with the laser pulse, the  $\text{CH}_3\text{OHF}^-$  signal decreases instantaneously (i.e., faster than the millisecond time resolution of the ICR) and then rises on a bimolecular time scale until the original signal intensity in the absence of irradiation is quantitatively recovered. This bimolecular increase in the  $\text{CH}_3\text{OHF}^-$  signal following the laser-induced dissociation is due to the reaction of the photoproduct  $\text{F}^-$  with excess methyl formate to regenerate  $\text{CH}_3\text{OHF}^-$ . Figure 4 shows the time dependence of the  $\text{CH}_3\text{OHF}^-$  signal in the presence and absence of irradiation with the double-resonance oscillator set to eject  $\text{F}^-$  during and after the laser pulse. Upon irradiation the  $\text{CH}_3\text{OHF}^-$  signal decreases unimolecularly and does not recover at all. Methanol is assumed to be the neutral product in the photodissociation, based on mass balance and thermochemistry.

Reaction 2 is reported<sup>21</sup> to be exothermic by 15 kcal mol<sup>-1</sup> and  $\text{F}^-$  generated from  $\text{NF}_3$  may contain up to 9 kcal mol<sup>-1</sup> of excess translational energy.<sup>23</sup> Thus, up to 24 kcal mol<sup>-1</sup> of excess internal energy is available to  $\text{CH}_3\text{OHF}^-$  formed via reactions 1 and 2. As a result,  $\text{CH}_3\text{OHF}^-$  formed in this manner may well be chemically activated to some degree. This conjecture was investigated by measuring the IR photodissociation yield at fixed laser fluence and wavelength as a function of two parameters: the total neutral gas pressure [M] and the time delay,  $\tau$ , between the grid pulse which initiates ion formation and the laser pulse. When either [M] or  $\tau$  is increased, the  $\text{CH}_3\text{OHF}^-$  ions will undergo more collisions on the average between the time they are formed via reaction 2 and the time they are photodissociated by the laser pulse. Since it is reasonable to expect that ions which already contain excess vibrational energy will dissociate more easily than ions which are thermalized (vide infra), a study of the IR multiphoton dissociation yield as a function of collisions prior to irradiation should be a probe for excess vibrational energy and its rate of loss from the ions.<sup>3</sup>

The number of ion-molecule collisions,  $N_{\text{coll}}$ , occurring during time  $\tau$  is given by eq 4, where  $k_i$  is the ion-molecule collision rate

$$N_{\text{coll}} = \sum_{i=1}^n k_i [\text{M}_i] \tau \quad (4)$$

constant between  $\text{CH}_3\text{OHF}^-$  and neutral gas  $i$ , calculated from ADO theory,<sup>24</sup> and  $[\text{M}_i]$  is the number density of neutral gas  $i$ . In our experiment two neutral gases,  $\text{NF}_3$  and methyl formate, are present in significant concentrations. Figure 5 shows the results of this study plotted as photodissociation yield vs.  $N_{\text{coll}}$ , where  $N_{\text{coll}}$  is calculated from eq 4 by knowing the partial pressures of each neutral gas, the appropriate ADO rate constants, and the delay time between the grid and laser pulses. Because all of the  $\text{CH}_3\text{OHF}^-$  ions are not formed during the grid pulse, eq 4 with

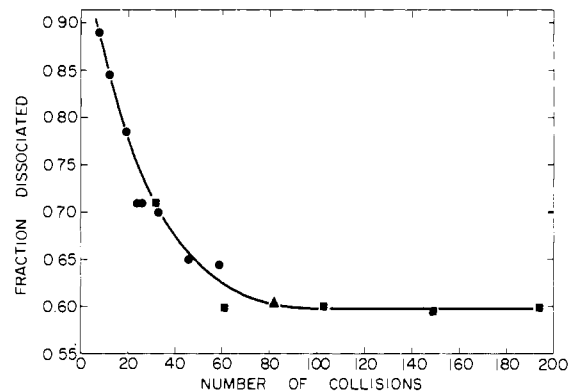
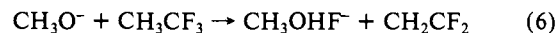
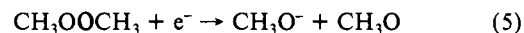


Figure 5. Dependence of the  $\text{CH}_3\text{OHF}^-$  photodissociation yield on the number of collisions undergone by the ion during the time between the grid and laser pulses (irradiation wavelength is 1072 cm<sup>-1</sup> at a fluence of 7 J/cm<sup>2</sup>): (●), pressure =  $4.0 \times 10^{-7}$  torr; (■) pressure =  $1.3 \times 10^{-6}$  torr; (▲) pressure =  $5.0 \times 10^{-6}$  torr.

$\tau$  defined as the time between the grid and laser pulses gives a maximum value of  $N_{\text{coll}}$ . When  $\text{CH}_3\text{OHF}^-$  has undergone relatively few collisions prior to irradiation, the photodissociation yield is 90% but decreases smoothly to 60% as more collisions intervene prior to irradiation. The most plausible explanation for this behavior is that  $\text{CH}_3\text{OHF}^-$  formed via reaction 2 does contain some excess vibrational energy which is removed by collisional energy transfer to the neutral bath gases.

For these results to be checked further,  $\text{CH}_3\text{OHF}^-$  was formed in an alternative manner<sup>25</sup> via reactions 5 and 6. Reaction 6 is



only 7 kcal mol<sup>-1</sup> exothermic,<sup>25</sup> and the neutral fragment  $\text{CH}_2\text{CF}_2$  might be expected to carry away a substantial fraction of that energy. Indeed, we find that the dissociation yield for  $\text{CH}_3\text{OHF}^-$  formed via reaction 6 is approximately 60%, independent of pressure or delay time between grid and laser pulses under the same photolysis conditions employed in obtaining the data in Figure 5.

It is difficult to interpret the data in Figure 5 quantitatively in terms of the number of collisions required to relax  $\text{CH}_3\text{OHF}^-$  formed via reaction 2 since all the  $\text{CH}_3\text{OHF}^-$  is not formed instantaneously at  $t = 0$ . It is, however, apparent that a substantial number (40–80) of ion-molecule collisions are required to remove enough excess energy so that the photodissociation yield becomes constant. These results suggest that by forming  $\text{CH}_3\text{OHF}^-$  via reaction 2 and employing low pressures and short delay times between the grid and laser pulses, we can study the IR photodissociation of chemically activated  $\text{CH}_3\text{OHF}^-$ . By working at higher pressures and longer delay times, we can study the IR photodissociation of collisionally relaxed  $\text{CH}_3\text{OHF}^-$ . Typical conditions employed in studying chemically activated ions were pressures of  $4 \times 10^{-7}$  torr and a delay time between the grid and laser pulses of 300 ms. Typical conditions employed in studying relaxed  $\text{CH}_3\text{OHF}^-$  were pressures of  $5 \times 10^{-6}$  torr and delay times of 500 ms. All data reported below were obtained on  $\text{CH}_3\text{OHF}^-$  formed via reactions 1 and 2.

The photodissociation spectrum of  $\text{CH}_3\text{OHF}^-$  was measured for both activated and relaxed ions. These spectra are shown in Figure 6. The results are presented as photodissociation cross section vs. wavelength. For this purpose, a phenomenological photodissociation cross section,  $\sigma$ , was defined in terms of the measured laser fluence,  $F$ , and the ratio of signal intensities in the presence and absence of irradiation,  $I/I_0$ . This definition of  $\sigma$  is given by eq 7. Equation 7 is expected to be a useful approximation in the limit of substantial decomposition per pulse.

$$-\ln(I/I_0) = \sigma F \quad (7)$$

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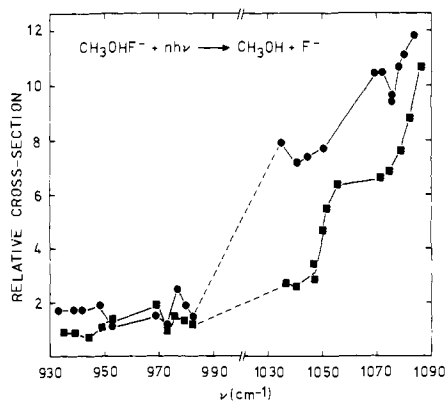


Figure 6. Infrared photodissociation spectra of chemically activated (●) and collisionally relaxed (■)  $\text{CH}_3\text{OHF}^-$ .

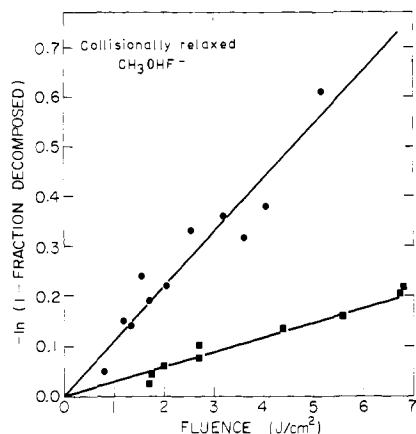


Figure 7. Fluence dependence of the IR photodissociation yield for collisionally relaxed  $\text{CH}_3\text{OHF}^-$ . The irradiation wavelength is  $1072\text{ cm}^{-1}$  (●) and  $939\text{ cm}^{-1}$  (■). The solid lines are linear least-square fits to the data.

The dependence of the photodissociation yield on laser fluence for activated and relaxed ions was investigated at two laser wavelengths,  $1072\text{ cm}^{-1}$ , which is near the maximum in the photodissociation spectrum, and  $939\text{ cm}^{-1}$ . Figure 7 shows the dependence of yield on laser fluence for relaxed  $\text{CH}_3\text{OHF}^-$ , and Figure 8 shows the dependence of yield on fluence for chemically activated  $\text{CH}_3\text{OHF}^-$ . The data are plotted in the semilogarithmic representation discussed previously.<sup>1,4,26</sup> Fluence dependences were obtained by attenuating the normal  $\text{CO}_2$  laser pulse, which consists of a 150-ns spike followed by a lower intensity tail lasting to 3  $\mu\text{s}$ . In order to check for possible intensity effects, we compared the yield obtained with the 3- $\mu\text{s}$  pulse, at constant fluence, to the yield obtained with a 200-ns pulse obtained by removing the  $\text{N}_2$  from the laser gas mixture. Over the fluence range accessible for comparison (0.1–1.0  $\text{J cm}^{-2}$ ) no measurable dependence on intensity was found for chemically activated  $\text{CH}_3\text{OHF}^-$ . Variable intensity data could not be obtained for relaxed  $\text{CH}_3\text{OHF}^-$  since the fractional decreases were too small to be accurately measured at the maximum fluence available with the short laser pulse.

### Discussion

The data presented in Figure 5, along with the absence of any pressure or delay time dependence of the photodissociation yield for  $\text{CH}_3\text{OHF}^-$  formed from methoxide and 1,1,1-trifluoroethane, are consistent with the hypothesis that  $\text{CH}_3\text{OHF}^-$  formed in the reaction of fluoride with methyl formate contains some excess vibrational energy. Since an ion with excess vibrational energy is closer to the dissociation threshold and has a higher density of rovibrational states to facilitate further photon absorption than an ion which is thermalized at the temperature of the ICR, it is

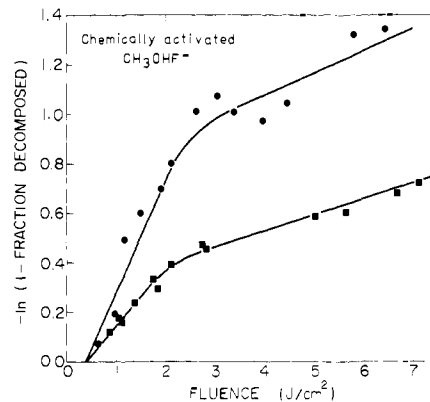


Figure 8. Fluence dependence of the IR photodissociation yield for chemically activated  $\text{CH}_3\text{OHF}^-$ . (irradiation wavelength is  $1072\text{ cm}^{-1}$ ) (●) and  $939\text{ cm}^{-1}$  (■).

quite reasonable that the excited ion should undergo IR multiphoton dissociation more readily than the thermalized ion. This effect has been observed for at least one other ion thus far<sup>3</sup> and has been demonstrated for neutrals in a study of chromyl chloride prepared with excess vibrational energy by internal conversion of an excited electronic state.<sup>27</sup>

The degree of internal excitation in  $\text{CH}_3\text{OHF}^-$  formed via reaction 2 cannot be determined in our experiment nor can a vibrational relaxation rate constant be easily extracted from the data in Figure 5, since as noted above, the  $\text{CH}_3\text{OHF}^-$  is not formed sufficiently rapidly compared to the time between nonreactive ion-molecule collisions. Nonetheless these data do indicate that the collisional relaxation process, with methyl formate as the major component of the bath gas, requires tens of collisions. The result that the collisional relaxation of a vibrationally excited ion requires so many collisions is somewhat surprising, given the strong attractive potential operative in ion-molecule collisions which, at thermal energies, leads to the formation of long-lived collision complexes<sup>28</sup> in which energy might be efficiently exchanged between collision partners.<sup>29</sup> While a number of studies<sup>30</sup> of stabilization vs. decomposition ratios for chemically activated ions have provided information on relative collisional relaxation efficiencies for different bath gases, thus far very little is known about the absolute relaxation rates. Asubiojo et al. found<sup>31</sup> that vibrational excitation in  $\text{Cl}_2^-$  survives hundreds of ion-molecule collisions. Similarly, Huber et al. have observed<sup>32</sup> long-lived vibrational excitation in  $\text{NO}_2^-$ . Kim and Dunbar have reported<sup>9</sup> that as many as 50 ion-molecule collisions may be required to partially relax vibrationally excited  $\text{C}_6\text{H}_5\text{Br}^+$ , and Jasinski and Brauman<sup>3</sup> have concluded that, depending on the bath gas employed, as few as 7 or as many as 30 ion-molecule collisions are required to relax vibrationally excited  $\text{CF}_3\text{O}^-$ . These results, in conjunction with the data presented above for  $\text{CH}_3\text{OHF}^-$ , indicate that, even for polyatomic ions in the presence of polyatomic neutral colliders, vibrational relaxation can be rather slow compared to the ion-molecule collision rate. Such results may have important implications for experiments designed to measure equilibrium properties and threshold properties in gas-phase ionic systems.

Two observations can be made regarding the multiphoton dissociation spectra of  $\text{CH}_3\text{OHF}^-$  shown in Figure 6. First, the photodissociation spectrum of chemically activated  $\text{CH}_3\text{OHF}^-$  appears somewhat broadened relative to that for the collisionally relaxed ion. This is consistent with the finding that the normal

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IR absorption spectrum of a gas-phase molecule tends to broaden with increasing temperature.<sup>33</sup> It does not require, however, that the chemically activated  $\text{CH}_3\text{OH}^-$  ions be characterized by a temperature. Second, the photodissociation spectra of both activated and relaxed  $\text{CH}_3\text{OH}^-$  are similar to the IR absorption spectrum of methanol, which has a strong absorption near  $9.4 \mu\text{m}$ . This vibrational transition in methanol is identified predominantly with the carbon-oxygen stretching motion. These results indicate that, at least in this instance, chromophoric character may be preserved in the multiphoton dissociation spectrum and that IR spectra of structurally similar neutral molecules can provide insight as to whether an ion will absorb in the  $\text{CO}_2$  laser region of the spectrum.

The fluence dependence data in Figures 7 and 8 are plotted by using the semilogarithmic representation suggested by Quack.<sup>26</sup> The normal shape of such plots for molecules for which IR multiphoton dissociation can be well described by using a simple master equation model with a single set of absorption/stimulated emission rate constants is a nonlinear concave upward portion at low fluence (incubation period) followed by a linear portion at higher fluence (steady-state regime).<sup>26,34</sup> The general type of master equation which gives rise to this behavior is well preceded in the literature<sup>34-38</sup> and has been used successfully in modeling the IR multiphoton dissociation of a number of molecules, including  $\text{SF}_6$  and  $\text{CF}_2\text{HCl}$ . The significance of the linear portion of plots of  $-\ln(1 - F_D)$  vs. laser fluence in Quack's formalism is that it can be used to extract a phenomenological photodissociation cross section and thus provides an experimentally accessible parameter which can be used to characterize data.<sup>1,26,34,39</sup> While the data for relaxed  $\text{CH}_3\text{OH}^-$  (Figure 7) appear to exhibit normal behavior (vide infra, however), the data for chemically activated  $\text{CH}_3\text{OH}^-$  (Figure 8) clearly do not. Rather, the plots at both wavelengths examined are concave downward. This saturation behavior begins at about  $2.5 \text{ J cm}^{-2}$  in both cases. We use the term saturation to refer to the marked decrease in slope of the plots in Figure 8.

To a good approximation the data in Figure 8 can be fit by using two straight line segments. Thus, the IR photodissociation of chemically activated  $\text{CH}_3\text{OH}^-$  can be characterized by at least two different phenomenological cross sections at each irradiation wavelength. This suggests that chemically activated  $\text{CH}_3\text{OH}^-$  undergoes IR multiphoton dissociation via two distinct absorption mechanisms, or, equivalently, that the ensemble of ions consists of two population components which photodissociate with different cross sections. The two photodissociation mechanisms can be characterized as an efficient or resonant absorption process, represented by that population component with the larger cross section (steeper slope in Figure 8) at a given wavelength, and a less efficient background or continuum absorption process, represented by the component with the smaller cross section. The curves in Figure 8 were drawn by fitting linear least-squares lines to the two linear portions at each wavelength and connecting these with an arbitrary curve in order to emphasize the saturation behavior. In order to extract effective cross sections for the two population components, however, we have fit the data at each wavelength to a biexponential of the form

$$1 - F_D = A_0 \exp(-\sigma_A F) + B_0 \exp(-\sigma_B F) \quad (8)$$

using Bevington's nonlinear least-squares routine,<sup>40</sup> CURFIT. In

Table I. Photodissociation Cross Sections for  $\text{CH}_3\text{OH}^-$ 

$\lambda$ , $\text{cm}^{-1}$	chemically activated $\text{CH}_3\text{OH}^-$				relaxed $\text{CH}_3\text{OH}^-$	
	$A_0$	$10^{21} \sigma_A$ , $\text{cm}^2$	$B_0$	$10^{21} \sigma_B$ , $\text{cm}^2$	$\lambda$ , $\text{cm}^{-1}$	$10^{21} \sigma$ , $\text{cm}^2$
1072	0.72	30.9	0.28	2.3	1072	2.2
939	0.46	18.3	0.54	0.80	939	0.6

eq 8  $F_D$  is the fractional decomposition per pulse,  $A_0$  and  $B_0$  denote the relative initial populations of the two components,  $\sigma_A$  and  $\sigma_B$  are the corresponding photodissociation cross sections, and  $F$  is the laser fluence. The populations and their cross sections are given in Table I along with the cross sections for relaxed<sup>41</sup>  $\text{CH}_3\text{OH}^-$ , determined from the slope of a linear least-squares fit to the data in Figure 7.

A possible trivial source of the effect might be poor overlap between the ion cloud and the laser beam. However, the fact that the saturation behavior is different at different wavelengths for  $\text{CH}_3\text{OH}^-$  combined with the fact that plots of  $-\ln(1 - F_D)$  vs. fluence are linear to above 90% decomposition for other ions in our apparatus<sup>1</sup> exclude this explanation.

A straightforward explanation of the differences between the two population components of the chemically activated  $\text{CH}_3\text{OH}^-$  might be that the two populations simply differ in internal energy. A second explanation might be that there are in fact two isomers of  $\text{CH}_3\text{OH}^-$  which photodissociate at different rates. Neither of these explanations is sufficient to account for all of the experimental observations, however. The data in Table I show that for chemically activated  $\text{CH}_3\text{OH}^-$  the fraction of the population associated with the resonant absorption mechanism,  $A_0$ , changes significantly with laser wavelength. This indicates that the two absorption mechanisms are not differentiated *solely* by differences in the internal energy of the  $\text{CH}_3\text{OH}^-$  population components  $A_0$  and  $B_0$ . If internal energy effects were the *only* factor responsible for differentiating the two population components, the observed photodissociation cross sections might depend on irradiation wavelength, but *the fractional populations associated with each component would have to be independent of wavelength*. This follows because the internal energy distribution of the  $\text{CH}_3\text{OH}^-$  is determined exclusively by the dynamics of reaction 2 and subsequent relaxation processes and is totally independent of any laser parameters such as wavelength. The same argument excludes the possibility of two isomers, since again, the relative amounts of each isomer must be independent of laser parameters. Although we can discount both of the simple explanations proposed above, we cannot determine with any certainty what the nature of the differences between the two population components is based on the available data. A possible origin of the differences between the two  $\text{CH}_3\text{OH}^-$  population components might involve the role of rotational energy effects in the IR photodissociation process. For example, at a given irradiation wavelength a specific subset of  $\text{CH}_3\text{OH}^-$  rotational states might be pumped efficiently to the dissociation threshold. If the wavelength is changed, a different, smaller or larger, subset of  $\text{CH}_3\text{OH}^-$  rotational states might be efficiently pumped. In either case, the remaining ions might photodissociate only via a less efficient absorption process. Such an explanation is, however, simply a hypothesis. In Figure 6, the spectrum for the activated ions reflects the resonant cross section at each wavelength since fluences below the onset of saturation were used in determining the cross sections.

Because of the observed saturation effect, the fluence dependence data for chemically activated  $\text{CH}_3\text{OH}^-$  are not consistent with a master equation model in which all of the ions respond to the laser field with the same set of single-photon absorption cross sections. This does not imply that the general features of this model such as the assumption of incoherent single-photon transitions with intensity proportional rate constants is invalid. Our result demonstrates only that the same set of rate constants need

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not apply to the entire ensemble of molecules. Subsequent to the preliminary publication of our observations,<sup>4</sup> considerable speculation concerning such behavior within the context of the master equation approach has appeared in the literature and several experimental examples have been suggested.<sup>34,42,43</sup> The case reported here for  $\text{CH}_3\text{OH}^-$  is particularly interesting because the saturation behavior in the fluence plots is quite dramatic and because the ions already contain excess vibrational energy prior to irradiation. Although the discussion presented above is given in terms of two population components for the chemically activated  $\text{CH}_3\text{OH}^-$ , the conclusions remain valid if more than two components are present. It is possible that chemically activated  $\text{CH}_3\text{OH}^-$  dissociates via three or more mechanisms but that the corresponding changes in slope in the plots in Figure 8 cannot be resolved. It is probably necessary, however, that there not be too wide a dispersion of subpopulations and rates or the sharp curvature would not be seen.<sup>34</sup>

The energetics of reaction 2, combined with an estimate of the density of internal states of  $\text{CH}_3\text{OH}^-$  as a function of energy, suggests that chemically activated  $\text{CH}_3\text{OH}^-$  is in the vibrational quasi-continuum.<sup>14a</sup> Two frequency experiments on neutrals have been interpreted as indicating that molecules in the quasi-continuum have relatively unstructured absorption spectra.<sup>14,44</sup> The results described above indicate that  $\text{CH}_3\text{OH}^-$  in the quasi-continuum can be characterized in terms of a resonant population component. This component varies in size and exhibits a different cross section for multiphoton dissociation depending on the irradiation wavelength. This result suggests that at least in this case some form of structure persists in the quasi-continuum, and it raises the interesting possibility of spectroscopically, and hence structurally, characterizing species near their dissociation thresholds via absorption or photodissociation spectroscopy.

Figure 7 shows that collisionally relaxed  $\text{CH}_3\text{OH}^-$  exhibits a linear plot of  $-\ln(1 - F_D)$  vs. fluence. However, we find that even this data cannot be fit quantitatively by using a simple master equation<sup>45a</sup> primarily because the experimental data remain linear

to such small fractional decomposition rather than showing an induction period. Such data can be fit if one invokes bottlenecks in the absorption mechanism;<sup>45b</sup> however, the physical interpretation of such an assumption is not clear at present.

### Conclusion

We have shown that IR photodissociation spectroscopy provides a useful technique for probing the collisional relaxation of internal energy in gas-phase ions. In the case of chemically activated  $\text{CH}_3\text{OH}^-$ , we find that 40–80 collisions are required for collisional relaxation. The photodissociation spectra of activated and relaxed  $\text{CH}_3\text{OH}^-$  indicate that the chromophoric character of conventional IR absorption spectra can be preserved, to some extent, in IR multiphoton dissociation spectra. The fluence dependence of the  $\text{CH}_3\text{OH}^-$  photodissociation yield was examined. In the case of activated  $\text{CH}_3\text{OH}^-$ , saturation of the photodissociation yield with increasing fluence was observed. This result indicates that the IR photodissociation of this ion occurs via at least two distinct mechanisms, identified with resonant and continuum absorption. These mechanisms apply to ion population components that cannot differ simply in internal energy content or structure. A master equation model for IR multiphoton dissociation which assumes that all molecules in the sample respond similarly to the laser field is not consistent with these results. However, the deviation of these results from the predictions of such a model provides useful information on the mechanism of IR laser photoactivation. The observation that the fraction of ions which undergoes efficient photodissociation depends on the irradiation wavelength indicates that a species in the quasi-continuum can show structured IR absorption behavior.

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## Infrared Multiphoton Photodetachment of Negative Ions in the Gas Phase

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**Abstract:** Electron photodetachment induced by infrared multiphoton absorption under collisionless conditions has been observed for benzyl, allyl, 2,4-hexadienyl, cycloheptadienyl, and anilide anions in the gas phase. The variety of ions which exhibit this behavior suggests that vibrational photodetachment is a fairly general process for anions with low electron detachment thresholds and that, as in the case of vibrational autoionization of neutrals, a potential energy surface crossing is not required for autodetachment to occur.

This paper describes our work on electron photodetachment from negative ions induced by infrared multiphoton absorption. Infrared photoactivation typically results in adiabatic fragmentations,<sup>1</sup> i.e., dissociation processes occurring on the ground electronic state potential surface. The present work was motivated

by the hypothesis that, if the barrier to adiabatic bond cleavage was significantly larger than the thermodynamic electron detachment threshold, electron detachment might compete favorably with dissociation following multiphoton absorption. This situation is quite common, since electron affinities are often<sup>2</sup> less than 3 eV whereas bond energies<sup>3</sup> are of the order of 3–5 eV.

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