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H atom formation dynamics in the dissociation of CH_3-CF_2Cl (HCFC-142b) after UV and VUV laser photoexcitation

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Using the laser photolysis/laser-induced fluorescence (LIF) ''pump-and-probe'' technique, the dynamics of H atom formation in the photodissociation of CH_3-CF_2Cl (HCFC-142b) after excitation at 193 nm and the Lyman-α wavelength were studied under collision-free conditions in the gas-phase at room temperature. The H atoms produced were detected by $(2p\,^2P \leftarrow 1s\,^2S)$-LIF using tunable narrow-band Lyman-α laser radiation ($\lambda_{L_\alpha} \approx 121.6$ nm) generated by resonant third-order sum-difference frequency conversion of pulsed dye laser radiation. In the VUV photodissociation experiments the Lyman-α laser radiation was used both to photodissociate the parent molecules and to detect the produced nascent H atoms via laser induced fluorescence. The following quantum yields Φ_H for H atom formation were determined by a photolytic calibration method: $\Phi_H(193\,\text{nm}) = (0.06 \pm 0.02)$ and $\Phi_H(L_\alpha) = (0.53 \pm 0.12)$. From the measured H atom Doppler profiles the average H atom kinetic energy was determined to be $E_T(193\,\text{nm}) = (51 \pm 10)$ kJ/mol and $E_T(L_\alpha) = (72 \pm 4)$ kJ/mol, respectively. *© 1997 American Institute of Physics.* [S0021-9606(97)01027-1]

I. INTRODUCTION

Following the Montreal Protocol hydrochlorofluorocarbons (HCFCs) can be used, on a transitional basis, as replacements of the chlorofluorocarbons (CFCs), which are believed to be responsible for the dramatic stratospheric ozone reductions observed in the polar regions.[1] The HCFC compounds have at least one C–H bond and can therefore be oxidized by OH free radicals in the troposphere. Although this leads to shorter lifetimes compared to those of the CFC compounds, HCFCs still have the potential to lead to chlorine transportation to the stratosphere. Recently measurements of stratospheric profiles of CH_3-CF_2Cl (HCFC-142b), a principal replacement choice for CF_2Cl_2 (CFC-12) in, e.g., polystyrene foams,[2] were carried out and it was found that CH_3-CF_2Cl is not yet in equilibrium, due to the rapidly increasing emissions.[3] Therefore, besides atmospheric *in situ* observations detailed laboratory studies on the UV and VUV photochemistry of these compounds and in particular measurements of primary photochemical product branching ratios are clearly needed in order to assess their environmental impact.[4]

Optical absorption spectra in the UV and in the VUV were measured for a number of HCFCs[5] while, on the other hand, the product formation dynamics after excitation in this spectral region have only been studied for a limited number of HCFCs. Experiments on the UV photodissociation of $CHFCl_2$ (HCFC-21) were carried out by Yang, Felder, and Huber, who found, using the photofragment translational spectroscopy, that at a photolysis wavelength of 193 nm, C–Cl bond fission is the primary photochemical process.[6] In CHF_2Cl (HCFC-22) dissociation dynamics studies carried out by Melchior *et al.*, H atoms were observed besides Cl atom formation after photoexcitation at the same UV wavelength.[7] Using time-of-flight mass spectrometry (TOF-MS) in combination with (2+1) resonance-enhanced multiphoton ionization (REMPI) product detection, a $H/\{Cl(^2P_{3/2}) + Cl^*(^2P_{1/2})\}$ ratio of (0.19 ± 0.06) and an upper limit of 1% for the HCl elimination channel was determined. In recent experiments, Brownsword *et al.* investigated the H atom formation dynamics and determined quantum yields (Φ_H) for H atom formation after photoexcitation of CHF_2Cl, CH_3Cl, and CH_2Cl_2 at 193 nm and the Lyman-α wavelength(121.6 nm) and found that while in the 193 nm photolysis H atom formation is of minor importance only it becomes a major channel in the Lyman-α photolysis.[8]

In the present article we report on the extension of these studies in order to provide experimental dynamical quantities such as photolytic H atom yields and information about the energy partitioning in the UV (193 nm) and Lyman-α photolysis also for the CH_3-CF_2Cl molecule. The measured H atom formation yields (in particular the one measured at the Lyman-α wavelength[9]) will help to assess the relative importance of this photochemical product pathway in the stratosphere and can serve as an absolute calibration point for photodissociation experiments where only relative product branching ratios (e.g., $H/\{Cl+Cl^*\}$, H/HCl) can be measured.[10] A detailed comparison of the present results ob-

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tained under collision-free conditions with the results of earlier 147 and 123.6 nm photodecomposition studies carried out in a ''static'' apparatus in the pressure range $p_{CH_3-CF_2Cl}=3.6$–20.6 Torr[11–13] will be made. Possible primary photochemical fragmentation mechanisms will be discussed in the light of the present results.

II. EXPERIMENT

The photodissociation studies were carried out in a flow cell at mTorr level pressures using a setup which was used previously to investigate the H atom formation in the VUV photodissociation of CHF_2Cl,[8] chloromethanes,[14] and the reaction dynamics of bimolecular gas-phase reactions.[15] In the following a brief summary of the experimental method will be given.

CH_3–CF_2Cl (Messer Griesheim, purity >98%) was pumped through the cell at room temperature. As stated by the manufacturer the amount of R141b (CH_3–$CFCl_2$) in the sample was less than 0.1%, with the remaining impurity being CH_3–CF_3 which did not interfere. The water content was less than 5 ppm. In the 193 nm photodissociation studies the CH_3–CF_2Cl pressure in the cell was typically 50–100 mTorr, in the Lyman-α photolysis studies the pressure was 50–80 mTorr. For the calibration measurements at 193 nm, HCl (Messer Griesheim, 99.99%) and for the calibration measurements at the Lyman-α wavelength, H_2O (deionized and double distilled) was pumped through the reaction cell at pressures of typically 5–10 and 40–70 mTorr, respectively. The flow rates of CH_3–CF_2Cl and HCl were regulated by mass flow controllers, the H_2O flow was regulated using a glass valve.

In one part of the study a UV excimer laser operating with an ArF mixture (193 nm emission wavelength, pulse duration 15–20 ns) was used to photodissociate the parent molecules. A circular aperture was used to skim off a homogeneous part of the rectangular excimer laser profile in order to provide the photolysis beam. A cylindrical lens (1 m focal length) was used to slightly focus the photolysis beam. Pump laser intensities were typically between $4-10\ \mathrm{mJ/cm^2}$. The pump laser beam was determined to be essentially unpolarized, and it is therefore expected that any possible anisotropy of the photodissociation process would be largely averaged out.

Narrow-band VUV laser light—tunable around the H(121.567 nm) atom Lyman-α transition—was generated by resonant third-order sum-difference frequency conversion of pulsed-dye-laser radiation (pulse duration 15–20 ns) in a phase-matched Kr/Ar mixture[16] in order to detect the photolytically produced nascent H atoms via $(2p^2P\leftarrow 1s^2S)$ laser induced fluorescence (LIF). The maximum VUV energy which can be obtained with this method is about 20 μJ/pulse.[16(b)] However, in the present experiments the energy was considerably lower due to absorption processes in the cell windows and VUV optics and in all experiments the actual VUV laser intensity was reduced until the desired intensity dependence of the H atom LIF signal was obtained.

The photolysis laser beam was aligned so as to overlap the probe beam at right angles in the viewing region of the LIF detector. The delay time between the UV pump and VUV probe pulses was typically 80 ns (with a time jitter of about ±5 ns), which allowed the collision-free detection of the H atoms produced under the low-pressure conditions of the experiment. A delay time of 80 ns was chosen to avoid that pump and probe laser do overlap in time, which could lead to unwanted multiphoton photochemical processes. The quality of the spatial overlap of the pump and probe laser beams was checked in order to ensure that no photolytically produced H atoms can escape the detection region during the typical delay time of 80 ns. This was done by recording H atom Doppler profiles in the 193 nm photolysis of HCl at pump/probe delay times between 20 and 150 ns. HCl photolysis at 193 nm leads to very fast H atoms ($v_H \approx 19\,300$ m/s) and the invariance of the line shape, in particular the invariance of the area around the center of the profile (which originates from H atom with a velocity vector perpendicular to the probe laser propagation direction) is a very sensitive check for ''fly-out.'' H atom Doppler profiles measured in the 193 nm HCl photolysis were invariant against changes in the pump/probe delay time in the range between 20 and 150 ns. It can therefore be ruled out that the measured H atom yields we report for CH_3–CF_2Cl are affected by ''fly-out'' of photolytically produced H atoms.

In the two color (193 nm pump and Lyman-α probe) experiments, although the probe laser intensities were low, small contributions to the LIF signal from H atoms produced directly by the Lyman-α photolysis of CH_3–CF_2Cl and HCl, respectively, were observed. In order to be able to completely discriminate between this ''Lyman-α-background'' signal and that produced in the 193 nm photolysis, an electronically controlled mechanical shutter was inserted into the photolysis beam path. At each point of the H atom Doppler profile, signal was recorded first with the shutter open, and then with the shutter closed, the difference between the two signals representing the contribution from H atoms generated solely by the 193 nm photolysis laser pulse. This procedure is similar to the ''Lyman-α-background'' subtraction method extensively used in our recent H/D atom formation studies in the UV photolysis of HNCO/DNCO.[17]

In a second set of experiments, the Lyman-α VUV laser light was used to photodissociate the CH_3–CF_2Cl molecule as well as to detect the photolytically produced nascent H atoms within the same laser pulse. The duration of the laser pulse was about 15–20 ns. In all experiments care was taken to separate the Lyman-α VUV laser light from the unconverted fundamental laser beams. Therefore, a lens monochromator followed by a light baffle system was used. A bandwidth of 0.4 $\mathrm{cm^{-1}}$ was determined for the VUV radiation in separate experiments by measuring under thermalized conditions Doppler profiles of H atoms generated in a microwave discharge. The H atom LIF signal was measured through a band pass filter (ARC, model 122-VN-ID, $\lambda_{center}=122$ nm, FWHM=20 nm) by a solar blind photomultiplier (Hamamatsu model R1259). During all measurements the relative VUV laser beam intensity was monitored with an ad-

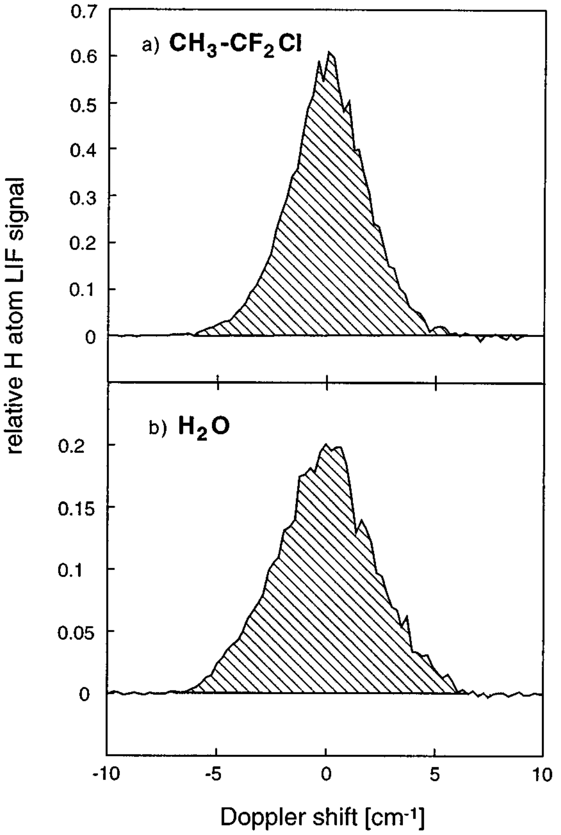

FIG. 1. H atom Doppler profiles obtained in the Lyman-α photolysis of (a) 57 mTorr of CH_3–CF_2Cl and (b) 45 mTorr of H_2O. The centres of the LIF spectra correspond to the H atom Lyman-α transition (82 259 cm^{-1}). Comparison of the total H atom signal (defined as the integrated area of the line profile) produced in the Lyman-α photolysis of CH_3–CF_2Cl with the signal observed in the case of H_2O is also shown. Details of the calibration method for the H atom quantum yield measurement in the CH_3–CF_2Cl photolysis are described in the text.

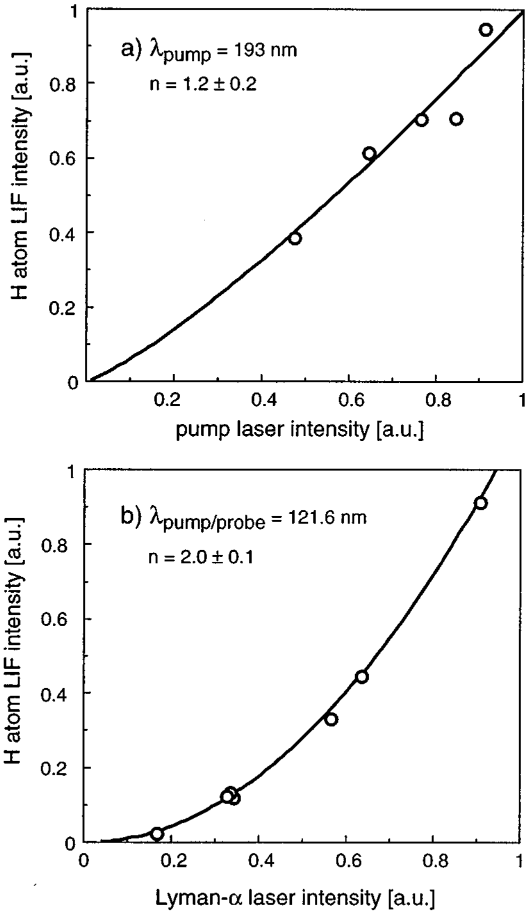

FIG. 2. (a) Dependence of the H atom LIF signal on the 193 nm photolysis (“pump”) laser and (b) dependence of the H atom LIF signal on the Lyman-α laser intensity in the CH_3–CF_2Cl photolysis experiments. In case of (b) the Lyman-α laser acts as “pump” and “probe” laser. Solid lines are the results of a fit to the experimental data to determine the power-dependence n of the H atom LIF signal. The obtained values for n are given in the figure.

ditional solar blind photomultiplier of the same kind. In order to obtain a satisfactory S/N ratio, each point of a recorded H atom Doppler profiles (as shown in Fig. 1) was averaged over 30 laser shots. Measurements were carried out at a laser repetition rate of 6 Hz. The LIF signal and UV photolysis and VUV probe beam intensities were recorded with a boxcar integrator system and then transferred to a microcomputer.

In the two color (UV pump–VUV probe) photodissociation studies care was taken that the observed H atom signals measured in the HCl and CH_3–CF_2Cl photolysis showed a linear dependence on the 193 nm pump laser [see Fig. 2(a)] and the probe laser intensities. In these experiments the H atom LIF signal was normalized point-by-point to the UV pump and Lyman-α VUV (probe) laser intensity.

In the one color (VUV pump–probe) experiments the H atom LIF signal was normalized point-by-point to the square of the Lyman-α VUV (pump/probe) laser intensity. Therefore, the $(n=1+1)$-photon nature (one-photon dissociation of the CH_3–CF_2Cl parent molecule followed by a one-photon H atom LIF-detection step) of the process was verified in separate experiments in which the intensity of the VUV laser radiation was varied. In Fig. 2(b) a plot of the measured H atom LIF signal versus the Lyman-α VUV laser intensity is shown for CH_3–CF_2Cl. Similar measurements were carried out in case of the H_2O Lyman-α photolysis, where for comparable experimental conditions a value of $n=(2.0\pm0.2)$ was observed. We therefore conclude that higher order processes like the secondary photodissociation of photolysis products can be neglected and need not be considered in the analysis and interpretation of the results.

III. RESULTS

A. Photolytic H atom quantum yields

Absolute quantum yields Φ_H for photolytic H atom formation were obtained by calibrating the H atom signal $S_H(CH_3–CF_2Cl)$ as measured in the CH_3–CF_2Cl photodissociation against the H atom signal $S_H(HCl/H_2O)$ from well-defined H atom number densities generated in the 193 nm photolysis of HCl and Lyman-α photolysis of H_2O, respectively. 193 nm photolysis of HCl generates H atoms with a quantum yield of unity and for the Lyman-α photolysis of H_2O an H atom quantum yield of $\Phi(H_2O)=1.02$ was determined.[18] In the Lyman-α photolysis experiments, for example, the H atom quantum yield was determined via the following equation:

$$\Phi_H(L_\alpha)=\gamma\{S_H(CH_3\text{–}CF_2Cl)\Phi(H_2O)\sigma_{H_2O}p_{H_2O}\}/\{S_H(H_2O)\sigma_{CH_3\text{–}CF_2Cl}p_{CH_3\text{–}CF_2Cl}\}. \qquad (1)$$

σ_{H_2O} and $\sigma_{CH_3\text{–}CF_2Cl}$ are the optical absorption cross sections of H_2O and CH_3–CF_2Cl at the Lyman-α wavelength. The optical absorption cross section for H_2O at the Lyman-α wavelength was measured in a previous study (where the H atom yield in the Lyman-α photolysis of methane was determined with a similar calibration method)[19] to be $\sigma_{H_2O}=(1.6\pm0.1)\times10^{-17}$ cm^2. The Lyman-α absorption cross sections $\sigma_{CH_3\text{–}CF_2Cl}=(3.1\pm0.2)\times10^{-17}$ cm^2 was also measured in the course of the present experiments and was found to be in very good agreement with the results of earlier measurements.[5(d)] S_H are the integrated areas under the measured H atom Doppler profiles (see, e.g., Fig. 1) and p_{H_2O} and $p_{CH_3\text{–}CF_2Cl}$ are the pressures of H_2O and CH_3–CF_2Cl, respectively. For the evaluation of the 193 nm photolysis experiments $\Phi(H_2O)$, p_{H_2O}, σ_{H_2O}, and $S_H(H_2O)$ have to be replaced by the corresponding HCl values. Literature values of $\sigma_{HCl}=(8.1\pm0.4)\times10^{-20}$ cm^2 and $\sigma_{CH_3\text{–}CF_2Cl}=0.53\times10^{-20}$ cm^2 for the optical absorption cross sections at 193 nm were used.[20,5(c)] In Eq. (1), the factor γ is a correction which accounts for the different degrees of absorption of the Lyman-α laser radiation by CH_3–CF_2Cl, HCl, and H_2O, respectively.

In the 193 nm photolysis studies the experimental data set which was evaluated consisted of 13 H atom profiles obtained in 6 independent calibration measurements in combination with 8 ''HCl calibration lines.'' The H atom quantum yield in the Lyman-α photolysis was evaluated using 10 H atom profiles measured in 5 independent calibration runs where 8 ''H_2O calibration lines'' were recorded. All the profiles had a S/N ratio similar to the profiles shown in Figs. 1 and 3. The quoted errors were determined from the 1σ statistical uncertainties of the experimental data, the uncertainties of the measured optical absorption cross sections, and in case of $\Phi_H(L_\alpha)$, from the uncertainty of the H atom quantum yield of water (estimated to be 20%) using simple error propagation. The following values for the H atom quantum yields were obtained: $\Phi_H(193\text{ nm})=(0.06\pm0.02)$ and $\Phi_H(L_\alpha)=(0.53\pm0.12)$.

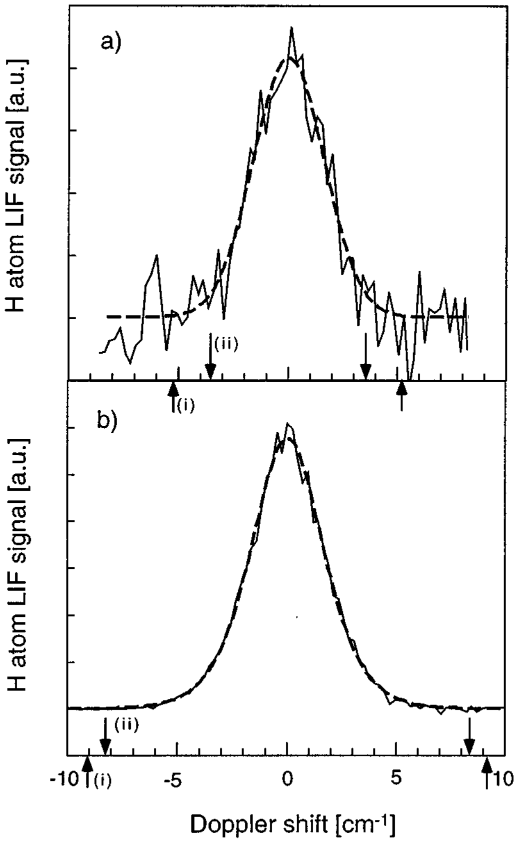

FIG. 3. H atom Doppler profiles obtained in the dissociation of CH_3–CF_2Cl after photoexcitation at (a) 193 nm and (b) at the Lyman-α wavelength (121.6 nm). The dashed lines represent results of a fit using a symmetric double sigmoidal function (for details see the text). Arrows indicate the maximum possible H atom Doppler shifts for the $\cdot CH_2$–CF_2Cl+H(i) and CH_2=CF_2+H+Cl(ii) product channels.

B. Average H atom translational energies

The measured H atom Doppler profiles were analysed in order to determine the average kinetic energy. Because the measured Doppler profiles directly reflect, via the linear Doppler shift $\nu-\nu_0=v_z\nu_0/c$, the distribution of the velocity component v_z of the absorbing atoms along the propagation direction of the probe laser beam, for an isotropic velocity distribution the average H atom kinetic energy is given by $E_T=3/2\, m_H\langle v_z^2\rangle$, where $\langle v_z^2\rangle$ represents the second moment of the laboratory velocity distribution $f(v_z)$ of the photolytically produced H atoms. The velocity distribution $f(v_z)$ was determined by fitting the measured H atom line shapes using a symmetric double sigmoidal function.[21] The results of the least-squares fit procedure are shown in Fig. 3. The analysis of the results revealed that all the H atom line shapes obtained in the 193 nm photolysis experiments can be well described by a symmetric double sigmoidal function which very closely resembles a Gaussian. For the H atom line shapes obtained in the Lyman-α photolysis this was not the case. Here, the use of a Gaussian fit function would lead to a systematic trend in the residuals of the fit[21(c)] in particular in the wings of the measured profiles and, as a consequence, later in the evaluation to an underestimation of the average H atom kinetic energy of about 25%.

Calculation of the second moments of $f(v_z)$ gave the following values for the average H atom kinetic energies: $E_T(193\text{ nm})=(51\pm10)$ kJ/mol and $E_T(L_\alpha)=(72\pm4)$ kJ/mol. The quoted error represents the 1σ statistical uncertainty obtained in the evaluation of the complete experimental data set. 13 H atom profiles measured in the 193 nm photolysis and 10 measured in the Lyman-α photolysis were

TABLE I. Reaction enthalpies $\Delta H_R(298\ \mathrm{K})$ of product channels in the dissociation of CH_3–CF_2Cl which are discussed in the text. Available energies to the products were calculated via $E_{\mathrm{avl}}(\lambda_{\mathrm{pump}})=\hbar\omega(\lambda_{\mathrm{pump}})-\Delta H_R(298\ \mathrm{K})$. Values are given in kJ/mol. Thermochemical data are from Ref. 24.

Product channel	$\Delta H_R(298\ \mathrm{K})$	E_{avl}: 193 nm	147 nm[a]	123.6 nm[a]	121.6 nm
$\cdot CH_2$–CF_2Cl+H	438.7	180.2	375.1	529.1	545.3
$CH_2{=}CF_2+H+Cl$	535.3	83.6	278.5	432.6	448.8
$CH_2{=}CF_2+H+Cl^*$ [b]	544.9	73.9	268.9	423.0	439.2
$CH_2{=}CF_2+HCl$	103.7	515.2	710.1	864.2	880.4

[a] Wavelengths used in the static decomposition studies of Ref. 11 and 12, respectively.

[b] The heat of formation of Cl* was calculated from the Cl value using $\Delta E=0.1$ eV (9.64 kJ/mol) for the $Cl(^2P_{1/2-3/2})$ spin–orbit splitting.

evaluated. In the evaluation of the H atom profiles it has to be taken into consideration that the measured line shape represents a convolution of the VUV laser spectral profile and the Doppler profile of the absorbing atoms. However, the measured probe laser bandwidth of our VUV laser system is so small that a back-correction due to the finite probe laser bandwidth was well below the experimental uncertainty.

IV. DISCUSSION

The measured quantum yields demonstrate the increasing importance of photolytic H atom formation in the CH_3–CF_2Cl fragmentation in going from UV to VUV excitation wavelengths. A similar behaviour was observed in UV and VUV photodissociation studies of CHF_2Cl and chloromethanes[8,14,22] as well as in earlier CH_3I UV and VUV photolysis studies.[23]

A. Photolysis of CH_3–CF_2Cl at 193 nm

For CH_3–CF_2Cl, absorption of a 193 nm photon leads to an excitation in the first absorption band [denoted as *A* band in Ref. 5(a)], which originates from a $3p\pi\rightarrow\sigma^*$(C–Cl) valence shell transition, where $3p\pi$ is a lone pair orbital of the Cl and σ^* is an antibonding C–Cl/σ–MO. Therefore, it can be expected as suggested by Okabe[5(b)] that the initial excitation is localized in the C–Cl bond leading preferentially to the breaking of this bond. H atom formation can occur, however, after intramolecular redistribution of the excitation energy, either via a single C–H bond fission or via a three-body dissociation process in combination with Cl (or Cl*) atoms and 1,1-difluoroethylene ($CH_2{=}CF_2$) formation (see Table I). That both reaction channels would be consistent with the observed energy release into H atom translational energy can be seen in Fig. 3(a), where the H atom Doppler profile observed at the 193 nm photolysis wavelength is depicted; the arrows (i) and (ii) indicate the maximum possible Doppler shift for the above suggested two-body and three-body product channels. Reaction enthalpies and the values of the energies available to the products as listed in Table I were calculated using the heat of formations given in Ref. 24. The observed small H atom quantum yield, however, clearly indicates that H atom formation is only a minor product channel in the 193 nm photolysis of CH_3–CF_2Cl. The measured value for the H atom yield is in line with results obtained in photodissociation studies of CH_3Cl and CH_2Cl_2, where also rather small primary H atom yields were observed ($\Phi_H<0.02$) after *A* band excitation at 193 nm.[8]

B. Photolysis of CH_3–CF_2Cl in the VUV spectral region

In the 147 and in the 123.6 nm photolysis of static samples of CH_3–CF_2Cl, using gas chromatography for final product analysis, $CH_2{=}CF_2$ was found to be the major photodecomposition product[11,12] and the following yields were reported: $\Phi_{CH_2CF_2}(147\ \mathrm{nm})=(0.74\pm0.06)$ and $\Phi_{CH_2CF_2}(123.6\ \mathrm{nm})=(0.82\pm0.02)$.

From the known CH_3–CF_2Cl UV/VUV absorption spectrum[5(d)] it can be derived that at 147 nm, valence (*A* band) as well as to a certain extent Rydberg excitation (*B* Band) can occur.[25] At 123.6 nm and at the Lyman-α wavelength (121.6 nm) *D* band Rydberg excitation can occur as well.[5(a),5(d)] *B* band absorption can be attributed to a Rydberg process, related to a $(n_{\mathrm{Cl}}\rightarrow 4s)$ transition while *D* band absorption[26] originates from a $(n_{\mathrm{Cl}}\rightarrow 4p)$ Rydberg excitation.

Although, concerning the final photochemical products the results of the 147 and 123.6 nm photolysis studies were found to differ very little—the only photochemical process unambiguously assignable to the 123.6 nm wavelength was the opening of an additional minor reaction pathway leading to $CH_2{=}CFCl$ formation ($\Phi_{CH_2CFCl}=0.05$)[12]—the "stability" of the major product molecule $CH_2{=}CF_2$ was found to depend strongly on the excitation wavelength.[11,12] In the 147 nm studies at low sample pressures, $CH{\equiv}CF$ was observed as a product and its formation was attributed to a sequential process of the form[11]

$$CH_3\text{–}CF_2Cl\xrightarrow{h\nu}CH_3\text{–}CF_2Cl^*\rightarrow CH_2=CF_2^{\ddagger}+HCl \tag{2a}$$

$$CH_2=CF_2^{\ddagger}\rightarrow CH{\equiv}CF+HF \tag{2b}$$

$$CH_2=CF_2^{\ddagger}+M\rightarrow CH_z=CF_2+M. \tag{2c}$$

Here, "*" denotes the electronically excited state, and "‡" an internally excited electronic ground state molecule. Based on an extrapolation of the observed pressure dependence of the $\Phi_{CH_2CF_2}/\Phi_{CHCF}$ ratio to collison-free conditions it was suggested that most of the nascent $CH_2{=}CF_2^{\ddagger}$ molecules are formed with an average internal energy higher than the activation energy for HF elimination via reaction (2b).[11] As a consequence it was suggested that in the 147 nm photolysis the primary product HCl must be formed in reaction (2a) for the most part with insufficient energy to undergo further decomposition to yield H+Cl.

Despite the fact that after dissociative excitation at 123.6 nm a considerably higher amount of energy is available to the products, no pressure dependence of the final $CH_2{=}CF_2$ yield was found in that case.[12] In addition, considerably lower concentrations of $CH{\equiv}CF$ were observed in the 147 nm studies, and it was suggested that after excitation at 123.6 nm $CH_2{=}CF_2$ molecules are initially produced in an excited singlet state but are, under the pressure conditions of the experiment, very efficiently quenched to the electronic ground state with less internal energy than the activation energy required for subsequent HF elimination.

The quantum yield of (0.53 ± 0.12) for primary H atom formation as measured in the present study after excitation at the Lyman-α wavelength (121.6 nm) suggests, however, that a considerable amount of $CH_2{=}CF_2$ could be produced directly in its electronic ground state via a three-body dissociation process of the form

$$CH_3\text{–}CF_2Cl \xrightarrow{h\nu} CH_3\text{–}CF_2Cl^* \rightarrow CH_2{=}CF_2^{\ddagger} + H + Cl. \qquad (3)$$

In that case, the average H atom translational energy of 72 kJ/mol as determined in the present study sets a ''natural'' upper limit for the internal energy of the nascent $CH_2{=}CF_2^{\ddagger}$ molecules of $E_{\text{int}} \leqslant 376.8$ kJ/mol which is only slightly above the activation energy of $\epsilon_{\text{HF}} = 372$ kJ/mol[27] for HF elimination via Eq. (2b). In the calculation of the upper limit for E_{int} it was assumed that the Cl atoms are produced in the electronic ground state $(^2P_{3/2})$ with zero kinetic energy. Therefore, it can be expected that in the actual dissociation process only very few of the $CH_2{=}CF_2^{\ddagger}$ molecules produced by reaction (3) will have enough energy to undergo further decomposition by HF elimination. Thus the very small amount of $CH{\equiv}CF$ produced in the static photolysis experiments at 123.6 nm as well as the observed pressure independence of the $CH_2{=}CF_2$ yield would be consistent with the above suggested primary dissociation mechanism (3).

The H atom Doppler profiles as observed in the present study after excitation of $CH_3–CF_2Cl$ at the Lyman-α wavelength are similar to the ones observed in the Lyman-α photolysis of CH_2Cl_2 and $CHCl_3$[8(a)] where H atom formation has been suggested to proceed via a Herzberg I predissociation mechanism.[28] This dissociation mechanism is of an indirect type in which an internally highly excited reaction intermediate (indicated by †) can be formed by a nonadiabatic transition from the initial excited Rydberg state (*) to a dissociative state

$$CH_3\text{–}CF_2Cl^* \rightarrow CH_3\text{–}CF_2Cl^{\dagger} \rightarrow CH_2{=}CF_2^{\ddagger} + H + Cl. \qquad (4)$$

In case the dissociation process is dominated by the final state interaction[29] such a mechanism can lead to statistical product state distributions characterized by a ''temperature'' uniform for all product degrees of freedom.[30] Using the ''canonical'' statistical model of Baer *et al.*[31]—assuming equipartitioning of the available energy among the product degrees of freedom and treating the final fragmentation step of Eq. (4) as a simultaneous three-body process—a ''product temperature'' of $T \approx 3500$ K can be obtained. The fact that the experimentally observed average H atom translational energy $E_T(L_\alpha) = (72\pm4)$ kJ/mol is considerably higher than the statistical ''prior'' value of $3/2\ kT = 44$ kJ/mol might suggest that the actual dissociation process lies somewhere in between the statistical (strong coupling)[29(a)] and nonstatistical (direct rapid predissociation) limit.[32] However, for a more detailed understanding of the $CH_3–CF_2Cl$ UV and VUV photochemistry a more sophisticated theoretical dynamical treatment of the fragmentation process and more information about the electronically excited states involved in the fragmentation processes is clearly needed.

V. SUMMARY

Using the laser photolysis/laser-induced fluorescence ''pump-and-probe'' technique absolute quantum yields for photolytic formation of H atoms were determined after optical excitation of $CH_3–CF_2Cl$(HCFC-142b) at 193 nm and at the Lyman-α wavelength (121.6 nm). The measured quantum yields $\Phi_{\text{H}}(193\ \text{nm}) = (0.06\pm0.02)$ and $\Phi_{\text{H}}(L_\alpha) = (0.53\pm0.12)$ clearly indicate that H atom production is only a minor photochemical product channel in the UV photolysis but becomes a major product channel in the VUV photodissociation. The relatively high value of $\Phi_{\text{H}}(L_\alpha)$ suggests $CH_3–CF_2Cl$ to be an efficient precursor of translationally excited H atoms in the earth's stratosphere. In addition, the experimentally observed energy release into the H atom translational degree of freedom when combined with results from previous static photodecomposition experiments suggests that besides H atoms comparable amounts of atomic chlorine and internally excited $CH_2{=}CF_2$ molecules are produced in the Lyman-α photolysis of $CH_3–CF_2Cl$.

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[1] P. J. Crutzen, in *Physics and Chemistry of Upper Atmospheres*, edited by B. M. McCormac (Reidel, Dordrecht, 1973); M. J. Molina and F. S. Rowland, Nature (London) **249**, 810 (1974).

[2] E. Linak and P. Yau, *Chemical Economics Handbook* (SRI International, Menlo Park, CA, 1995).

[3] J. M. Lee, W. T. Sturges, S. A. Penkett, D. E. Oram, U. Schmidt, A.

Engel, and R. Bauer, Geophys. Res. Lett. **22**, 1369 (1995).

[4] *Scientific Assessment of Ozone Depletion: 1991*, World Meteorological Organization Global Research and Monitoring Project Report No. 25 (World Meteorological Organization, Geneva, Switzerland, 1992).

[5] (a) M. B. Robin, *Higher Excited States of Polyatomic Molecules*, Vol. 1 (Academic, New York, 1974); (b) H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978); (c) W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, No. 10* (NASA, JPL Publication 92-20, 1992); (d) J. Doucet, P. SaUVageau, and C. Sandorfy, J. Chem. Phys. **62**, 355 (1975).

[6] X. Yang, P. Felder, and J. R. Huber, Chem. Phys. **189**, 129 (1994).

[7] A. Melchior, P. Knupfer, I. Bar, S. Rosenwaks, T. Laurent, H.-R. Volpp, and J. Wolfrum, J. Phys. Chem. **100**, 13375 (1996).

[8] (a) R. A. Brownsword, M. Hillenkamp, T. Laurent, R. K. Vatsa, H.-R. Volpp, and J. Wolfrum, J. Phys. Chem. A **101**, 995 (1997); (b) J. Phys. Chem. A (to be published).

[9] For more details about the importance of the Lyman-α wavelength in the earth's stratosphere see, for example, R. P. Wayne, *Chemistry of Atmospheres*, 2nd ed. (Oxford University Press, Oxford, 1994).

[10] A. Melchior, I. Bar, and S. Rosenwaks (work in progress).

[11] T. Ichimura, A. W. Kirk, and E. Tschuikow-Roux, Int. J. Chem. Kinetics **9**, 697 (1977).

[12] T. Ichimura, A. W. Kirk, and E. Tschuikow-Roux, J. Phys. Chem. **81**, 2040 (1977).

[13] D. Salomon, A. W. Kirk, and E. Tschuikow-Roux, Int. J. Chem. Kinetics **9**, 619 (1977).

[14] R. A. Brownsword, M. Hillenkamp, T. Laurent, R. K. Vatsa, H.-R. Volpp, and J. Wolfrum, J. Chem. Phys. **106**, 1359 (1997).

[15] H.-R. Volpp and J. Wolfrum, in *Gas Phase Chemical Reaction Systems: Experiments and Models 100 Years after Max Bodenstein*, Springer Series in Chemical Physics, Vol. 61, edited by J. Wolfrum, H.-R. Volpp, R. Rannacher, J. Warnatz (Springer, New York, 1996).

[16] (a) G. Hilber, A. Lago, and R. Wallenstein, J. Opt. Soc. Am. B. **4**, 1753 (1987); (b) J. P. Marangos, N. Shen, H. Ma, M. H. R. Hutchison, and J. P. Connerade, *ibid*. **7**, 1254 (1990).

[17] R. A. Brownsword, M. Hillenkamp, T. Laurent, R. K. Vatsa, and H.-R. Volpp, J. Chem. Phys. **106**, 4436 (1997).

[18] T. G. Slanger and G. Black, J. Chem. Phys. **77**, 2432 (1982).

[19] R. A. Brownsword, M. Hillenkamp, T. Laurent, R. K. Vatsa, H.-R. Volpp, and J. Wolfrum, Chem. Phys. Lett. **266**, 259 (1997).

[20] Y. Mo, K. Tonkua, Y. Masum, M. Kawasaki, T. Sato, T. Arikawa, P. T. A. Reilly, Y. Xie, Y. Yag, Y. Huag, and R. J. Gordon, J. Chem. Phys. **97**, 4815 (1992).

[21] (a) R. D. Rundel, Photochem. Photobiol. **38**, 569 (1983); (b) R. D. Rundel, *Peakfit v2.0 Reference Manual* (Jandel Scientific, San Rafael, CA, 1989); (c) W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in C* (Cambridge University Press, Cambridge, 1988).

[22] K. Tonokura, Y. Mo, Y. Matsumi, and M. Kawasaki, J. Phys. Chem. **96**, 6688 (1992); Y. Matsumi, K. Tonokura, M. Kawasaki, G. Inoue, S. Satyapal, and R. Bersohn, J. Chem. Phys. **94**, 2669 (1991).

[23] R. E. Continetti, B. A. Balko, and Y. T. Lee, J. Chem. Phys. **89**, 3383 (1988); M. R. Levy and J. P. Simons, J. Chem. Soc. Faraday Trans. 2 **71**, 561 (1975).

[24] (a) R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data **21**, 1125 (1992); (b) C. F. Melius, Sandia National Laboratories, BAC-MP4 Heats of Formation Data File (Vers. July 16, 1996).

[25] In Ref. 12 it was suggested that in the 147 nm (Xe resonance line) photolysis studies (Ref. 11) the majority of the excited molecules could be of the Rydberg (*B* band) type. This was based on the fact that the extinction coefficient measured in the 147 nm experiments was considerably higher than the literature value which one would expect for valence (*A* band) excitation.

[26] Here, we follow the notation of Ref. 5(a), p. 157.

[27] J. M. Simmie and E. Tschuikow-Roux, J. Phys. Chem. **74**, 4075 (1970).

[28] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. III (Van Nostrand, Toronto, 1966).

[29] (a) M. Shapiro and R. Bersohn, Annu. Rev. Phys. Chem. **33**, 409 (1982); (b) R. Schinke, *Photodissociation Dynamics Spectroscopy and Fragmentation of Small Polyatomic Molecules* (Cambridge University Press, Cambridge, 1993), and references therein.

[30] S. M. Freund, G. A. Fisk, D. R. Hershbach, and W. Klemperer, J. Chem. Phys. **54**, 2510 (1971); J. L. Kinsey, J. Chem. Phys. **54**, 1206 (1971); A. Ben-Shaul, R. D. Levine, and R. B. Bernstein, Chem. Phys. Lett. **15**, 160 (1972); R. D. Levine and R. B. Bernstein, in *Dynamics of Molecular Collisions*, edited by W. H. Miller (Plenum, New York 1976), Vol. 2, Part B.

[31] T. Baer, A. E. DePristo, and J. J. Hermans, J. Chem. Phys. **76**, 5917 (1982).

[32] M. J. Berry, J. Chem. Phys. **61**, 3114 (1974).