AIP | The Journal of Chemical Physics

Cl2 and HCl emissions in the ArFlaser photolyses of chlorinated compounds: Identification and mechanism of generation

R. D. Kenner, H. K. Haak, and F. Stuhl

Citation: The Journal of Chemical Physics **85**, 1915 (1986); doi: 10.1063/1.451135
View online: http://dx.doi.org/10.1063/1.451135
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/85/4?ver=pdfcov
Published by the AIP Publishing

Cl_2 and HCl emissions in the ArF-laser photolyses of chlorinated compounds: Identification and mechanism of generation

R. D. Kenner, H. K. Haak,[a] and F. Stuhl
Physikalische Chemie I, Ruhr-Universität, D-4630 Bochum, West Germany

(Received 18 March 1986; accepted 2 May 1986)

The ArF (193.3 nm)-laser photolyses of several chlorinated methanes and $COCl_2$ were investigated using the unfocused beam. Cl_2 and HCl emissions from highly excited states were observed and identified by use of recently calculated potential energy curves. The emissions were generated by absorption of two ArF-laser photons. It was observed that the first absorbed photon forms an intermediate which subsequently absorbs the second photon to generate the fluorescent molecule. Some intermediates can also absorb a KrF-laser photon to yield Cl_2 emission. The intermediates were identified by energy restrictions to be Cl_2 with excitation energies below the dissociation limit. In the cases of $COCl_2$ and CCl_4 this excitation extends up to the dissociation energy of $Cl_2(X)$. Also, vibrationally hot ground state HCl molecules are formed as intermediates. In some cases the intermediates contain the total energy available from the first photolysis step. Energy considerations result in an estimate for the heat of formation of the CHCl radical.

I. INTRODUCTION

Photochemical dissociation rarely generates fragments in single excited states. Usually each fragment is produced in numerous energetically accessible states and often several sets of photofragments are possible. This distribution of product states frequently makes it difficult to characterize emissions produced by photolytic processes, particularly when the spectroscopy of the fragments is poorly known or an emission is observed for the first time or at low spectral resolution.

A few years ago not much was known about highly excited Cl_2 and HCl states.[1] Therefore, it is not surprising that a previous UV-laser photochemistry study on CCl_4 and CCl_3F[2] identified several UV emissions as originating from excited Cl_2 but did not assign the excited Cl_2 states. In preceding work, we had investigated the ArF excimer laser photolyses of some chlorinated methanes and had observed VUV emissions which we attributed to the formation of highly excited Cl_2 molecules being formed by absorption of at least two laser photons.[3] Additional confirmation for the generation of these highly excited Cl_2 states was subsequently obtained by studying a number of chlorinated species containing a variable number of Cl atoms.[4] Using this "chemical method of identification," we have observed strong VUV emissions in the ArF-laser photolysis of $COCl_2$ and $SOCl_2$, medium intensities for CCl_4 and $CHCl = CCl_2$, weak intensities for $CHCl_3$, $CFCl_3$, $CH_3–CCl_3$, and $CHCl_2–CHCl_2$, and very weak emissions in the photolyses of CH_2Cl_2, CF_2Cl_2, and $CH_3–CHCl_2$. For molecules containing only one Cl atom (CH_3Cl, $CH_3–CH_2Cl$) or no Cl atoms, no such VUV emission was observed.[3,4] In extension of that work, we have subsequently studied the emission occurring in the UV region for several selected chlorinated compounds[3] and have found several Cl_2 emissions[4] similar to those reported by Tiee *et al.*[2] for the photolysis of CCl_4. Additional emissions were observed for methanes containing both H and Cl.[4]

While that study[3,4] was performed much progress was achieved both by theoretical[5] and by experimental work[6–9] and preliminary assignments of the VUV and UV fluorescences were attempted at that time.[4] Since the completion of the present spectroscopic experiments, a report on the ArF-laser photolysis of $COCl_2$ has been published.[10] Our results and assignments differ in certain details with this report on $COCl_2$. For $COCl_2$, CCl_4, $CHCl_3$, and CH_2Cl_2, we will summarize our results pertinent to the formation of excited Cl_2 (and CO for $COCl_2$) and present support for the identification of the emissions observed in our experimental study. We will further describe an additional emission observed only in the photolyses of $CHCl_3$ and CH_2Cl_2, which we propose to be due to the formation of excited HCl. The discussion of these emissions will be assisted by some of the most recent experimental studies on the spectroscopy of Cl_2[6,7,11–17] and HCl[18–20] and theoretical work on HCl.[21,22]

We have recently learned to study the mechanisms of ArF-laser photolysis processes caused by absorption of two photons.[23] The pump and probe technique used for this purpose was also applied to the chlorinated methanes and $COCl_2$ to investigate the existence and nature of possible intermediate species. It will be shown that these experiments further help to identify the fluorescence emissions and furnish additional knowledge on the photochemistry of chlorinated compounds and on the spectroscopy of hot Cl_2 and HCl.

II. EXPERIMENTAL

The apparatus used to study the photolysis of chlorinated compounds has been previously described in detail.[3,4,23,24] Briefly, an unfocused ArF-excimer laser (193.3 nm, 6.415 eV; typically 50 mJ) was used to irradiate slowly flowing samples of chlorinated molecules. Fluorescence emissions were detected at right angles to the laser beam. Spectra were recorded in the wavelength range 120 to 350 nm using gratings blazed for 150 and 300 nm. The spectral resolution ranged from 0.4 to 4 nm depending on the fluorescence intensity. Decays of the emissions as short as 30 ns could be measured by a transient recorder. The pressures of the pho-

---

[a] Present address: Buck Chemische-Technische Werke, D-8230 Bad Reichenhall.

tolyzed gases usually were in the range from 13 to 40 Pa. In some of the experiments inert gases such as Ar, Kr, or N_2 were added at pressures up to 1.33×10^4 Pa.

The pump–probe experiments were performed in a similar manner to that described earlier.[23] For these experiments, a second excimer laser (lasing at 193 or 248 nm) along with the appropriate triggering units was added to the above apparatus. For those experiments designed to test for the existence of intermediates, the output of the photomultiplier was directly observed with a fast storage oscilloscope. For all other pump–probe experiments, i.e., recording spectra, measuring fluence dependencies, and preliminary measurements of the intermediate lifetimes, a boxcar averager with gated integrator (PAR 162/165) and a strip chart recorder were used to register the signal.

The gases were either taken from the gas phase of their liquids or from their storage vessels. The liquid (purity $\geqslant$99.8% for CCl_4, $\geqslant$99% for $CHCl_3$, and $\geqslant$99.7% for CH_2Cl_2) were thoroughly degassed. $COCl_2$ (purity $\geqslant$99.9%) was used as delivered.

III. RESULTS

Fluorescence emissions generated by photolyzing $COCl_2$, CCl_4, $CHCl_3$, and CH_2Cl_2 were recorded in both the VUV and UV region. As examples, the properties of the emissions obtained in the ArF-laser photolysis of $COCl_2$ and $CHCl_3$ will be presented here. The fluorescences observed for $COCl_2$ are the strongest and most structured of these emissions. The spectrum obtained from $CHCl_3$ displays an additional emission not reported before in the photolyses of chlorinated methanes. The identification of these emissions and the mechanisms of their production will be discussed in the next section.

Figure 1 displays two VUV spectra taken (A) for pure $COCl_2$ at 13 Pa using a resolution of 0.4 nm and (B) for 16 Pa $COCl_2$ and 93 Pa Kr using 1 nm resolution. Note that the intensity scales for both spectra are different. While all VUV spectra obtained for the other chlorinated compounds mentioned in the Introduction appear to be continuous as shown in Ref. 3, spectrum (A) consists of a continuum with superimposed structure. The short wavelength cutoff of the continuum was determined to be 141 ± 2 nm. Spectrum (B) indicates efficient quenching for both the continuum and the structured emission.

Two spectra observed for 13 Pa $COCl_2$ in the UV region are shown in Fig. 2, (A) for pure $COCl_2$ and (B) with the addition of 1.33×10^4 Pa Kr. Besides the emissions displayed in spectrum (A), fluorescence was observed at $\lambda\approx199$ nm (see also Fig. 3); this rapidly decreases towards shorter wavelengths. This decrease is probably due to decreasing sensitivity of the photomultiplier and to absorption by air present in the light path while the UV spectra were taken. As will be discussed later the most intense emissions in spectrum (A) originate from excited Cl_2. Upon addition of Kr to the system [spectrum (B)], the fluorescence at 308 nm and its accompanying progression towards shorter wavelengths are efficiently quenched. The fluorescence at 254 nm changes its shape and shifts slightly to longer wavelengths ($\lambda=258$ nm). Additionally, in the presence of Kr, emission of KrCl at 222 nm is generated. The same emissions, but weaker, were observed in the ArF-laser photolysis of CCl_4 in the UV region. In this case additional CCl ($A\,^2\Delta\rightarrow X\,^2\Pi$) emission was detected at 278 nm. This emission, which also occurs in the photolysis of $CHCl_3$ (Fig. 3) and weakly for CH_2Cl_2, will not be discussed further in the present work. The spectrum we obtained with CCl_4 is similar to that given by Tiee *et al.*[2] and will not be shown here.

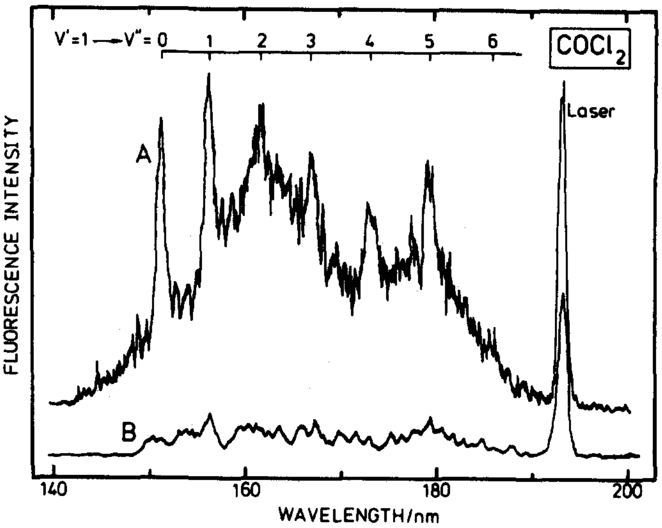

FIG. 1. VUV emission spectra generated in the ArF-laser photolysis of $COCl_2$. Spectrum (A): 13 Pa $COCl_2$, 0.4 nm resolution; spectrum (B): 16 Pa $COCl_2$ + 93 Pa Kr, 1 nm resolution. Spectrum (B) was recorded with half of the sensitivity (compare laser intensities at 193 nm). The location for the progression CO($A\,^1\Pi$, $v'=1\rightarrow X\,^1\Sigma^+,v''$) is indicated.

Figure 3 shows a spectrum obtained in the ArF-laser photolysis of 27 Pa $CHCl_3$. The most intense fluorescence in this spectrum is a broad, seemingly continuous emission at $\lambda\approx230$ nm which is not observed in the case of $COCl_2$ and CCl_4. Support will be given in the discussion for excited HCl molecules causing this fluorescence. The other emissions ($\lambda\approx199$, ≈254, 278, and 308 nm) are much weaker than

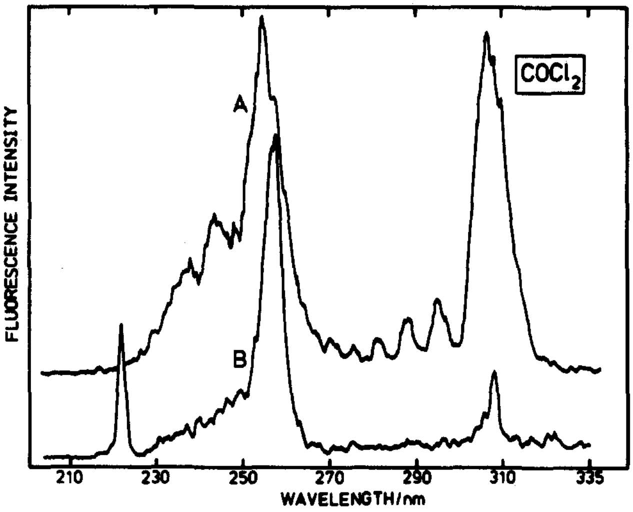

FIG. 2. UV spectra generated in the ArF-laser photolysis of $COCl_2$ using a resolution of 1 nm. Spectrum (A): 13 Pa $COCl_2$; spectrum (B): 13 Pa $COCl_2+1.33\times10^4$ Pa Kr.

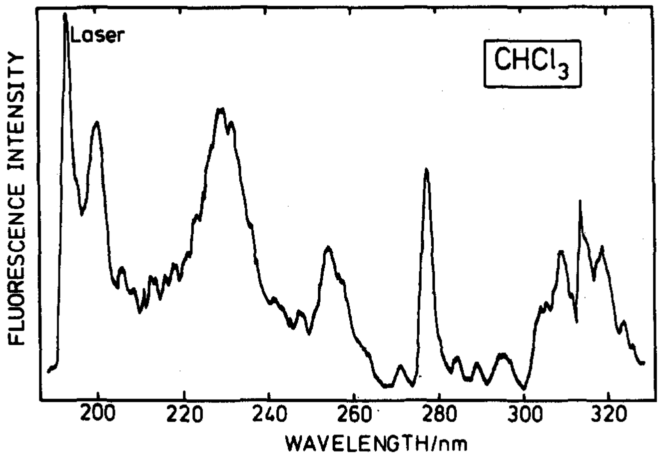

FIG. 3. UV spectrum observed in the ArF-laser photolysis of 27 Pa $CHCl_3$ using a resolution of 1 nm.

the corresponding ones generated from $COCl_2$ and CCl_4. At $\lambda = 315$ nm, probably $CH(C \rightarrow X)$ and additional HCl emission are generated. In the photolysis of CH_2Cl_2, the UV emissions are found to be much weaker than in the case of $CHCl_3$ and besides the CCl and $CH(C \rightarrow X)$ fluorescences, only low intensities of 230 and 199 nm emission were detected. When using large fluences, a sharp line was observed at 248 nm for the chlorinated methanes. This emission, which is generated by $C(^1D_2) + 193.1\ \text{nm} \rightarrow C(^1P_1)$ and $C(^1P_1) \rightarrow C(^1S_0) + 247.9$ nm, and the CH emission at 315 nm will not be discussed further in the present work.

The number of photons n absorbed to generate an emission was determined according to the equation $I_F = I_L^n$ where I_F and I_L are the intensities of the fluorescence and laser light, respectively. In these experiments using one ArF-laser, the values of n were found to be close to 2 ($\pm 10\%$) except for the $C(^1P_1 \rightarrow {}^1S_0)$ emission which gave $n = 2.3$ and the CCl emission which also gave a value significantly greater than two. All emissions were found to be short lived ($\tau < 30$ ns) at the pressures of the parent molecules (13 to 27 Pa) except for the CCl emission which lives longer than 110 ns (at 2.7 Pa).

The excitation of the emitting states for each of the emissions mentioned above required more than one photon. We have therefore performed pump–probe experiments using two excimer lasers to test the involvement of long-living (relative to the duration of the laser pulse) intermediates in the generation of each of the emissions. As described in earlier publications,[23] we test this involvement by comparing the intensity of the fluorescence generated by the probe laser alone with that generated with a preceding pump laser pulse. The involvement of an intermediate is signaled by an increase in intensity for the case in which the pump laser is fired. We find such an increase for each of the emissions observed between 140–320 nm in the ArF-laser photolysis of CH_2Cl_2, $CHCl_3$, CCl_4, and $COCl_2$. This also includes those emissions not specifically discussed in this paper; the CCl band at 278 nm, the CH band at 315 nm, and the C atom line at 248 nm.

Since intermediates were detected for all emissions, several further experiments were performed. First, the dependence of the enhanced emission on the fluence of each of the lasers was checked for the VUV emissions and the 254 nm band in the case of CCl_4. In both cases, $n = 1$ for each laser is observed. Second, preliminary lifetime measurements were performed for the VUV emission for CCl_4. With 2 Pa CCl_4, the measured lifetime of the intermediate for emission at 170 nm is about 50 μs. This lifetime is not corrected for diffusion or for quenching and the zero pressure lifetime is hence expected to be longer. Third, the probe laser was operated at 248 nm while the pump laser operated as usual at 193 nm. No emission was detected using the KrF laser alone. However, examination of the spectrum generated by the KrF probe laser when delayed 400 ns after the pump laser showed two bands in the spectral region between 160 and 320 nm for both CCl_4 and $CHCl_3$. These bands were the CCl band at 278 nm and the band at 254 nm. Scattered laser light at 248 nm masked any emission from C atoms but there was no emission at 193 nm. Finally, because of the finite duration of the laser pulses, the delay time could not be made significantly shorter than 100 ns. Within this limitation we have seen no increase in the intensity of the enhanced emission with increasing delay time between the lasers. This indicates prompt formation of the intermediate species during the pump laser pulse.

As indicated in Figs. 1 and 2, the quenching of the emissions was mostly studied in a qualitative fashion. In some experiments, up to 1.33×10^4 Pa N_2 or Kr was added to 13 to 27 Pa of $COCl_2$ or CCl_4 and the intensity decrease was measured at the wavelengths of the Cl_2 emissions. The quenching of most Cl_2 emissions was found to be very efficient. As has been shown in previous studies,[10,30] the fluorescence intensity around 258 nm increased when rare gases such as Ar and Kr were added. Furthermore, the peak intensity slightly moves towards longer wavelengths as is seen in Fig. 2. Upon addition of Kr to $COCl_2$, CCl_4, and $CHCl_3$, emission from KrCl was observed at 222 nm. No KrCl fluorescence was found for CH_2Cl_2. An example for the KrCl emission is given in the spectrum of Fig. 2(B).

V. DISCUSSION

Since all fluorescence emissions we observed are rather weak, the spectral resolution is necessarily poor and unfortunately, structure was found to be a rare feature. The following attempt to identify the origin of the emissions is assisted by calculated potential energy curves, by energy requirements and by previous work. Finally, we will discuss the mechanism of formation of the excited species on the basis of our pump and probe experiments.

To aid the discussion, Table I displays the energies available for excitation of the products by several selected processes [reactions (1)–(6)] which yield either Cl_2 or HCl. The available energies are listed for one-photon and two-photon absorption processes. For the fragments in each case, the formation of ground state molecules is taken into account in Table I. The relevant excitation energies of Cl_2, including the observed emissions, are shown in the potential energy diagram of Fig. 4.[5] In addition, Fig. 5 displays simplified potential energy curves of HCl.[21,22]

TABLE I. Dissociation energies D_0 and energies available for the excitation of the Cl_2 or HCl fragments in the one-photon [E(ArF)–D_0] and in the two-photon [$2E$(ArF)–D_0] ArF-laser photolysis of the parent molecule M.

Reaction	M	Photolysis products	D_0 (eV)[a,c]	E(ArF)–D_0[b,c] eV	$2E$(ArF)–D_0[b,c] eV
(1)	$COCl_2$	$CO + Cl_2$	1.08 ± 0.04	5.33 ± 0.05	11.75 ± 0.06
(2)	CCl_4	$CCl_2 + Cl_2$	3.43 ± 0.24	2.99 ± 0.24	9.40 ± 0.26
(3)	$CHCl_3$	$CHCl + Cl_2$	4.48 ± 0.45	1.93 ± 0.45	8.35 ± 0.47
(4)		$CCl_2 + HCl$	2.52 ± 0.23	3.89 ± 0.24	10.31 ± 0.25
(5)	CH_2Cl_2	$CH_2 + Cl_2$	4.92 ± 0.06	1.50 ± 0.07	7.91 ± 0.08
(6)		$CHCl + HCl$	3.43 ± 0.45	3.00 ± 0.45	9.40 ± 0.47

[a] All necessary values of enthalpies of formation, ΔH^0_{f0}, were taken from the summaries in Refs. 25–27. Dissociation into the lowest states is assumed; thermal energies are not taken into account.

[b] $E(\mathrm{ArF}) = (6.415 \pm 0.011)$ eV.

[c] The error limits represent accumulative errors.

A. VUV emissions

1. Structured fluorescence

As indicated in Fig. 1, the positions of the VUV-emission maxima correspond to the $CO(A\,^1\Pi, v' = 1 \rightarrow X\,^1\Sigma^+, v'' = 0\text{–}6)$ sequence. This assignment is further confirmed by the data in Table II where measured and tabulated[28] wavelengths, and intensities corrected for the appropriate wavelengths and Franck–Condon factors[29] are compared. Considering the uncalibrated optical detection system and the large varying absorption coefficient of $COCl_2$ in the VUV,[30] the Franck–Condon factors compare well with the intensity data. This assignment[4] is in agreement with that obtained by Wilson *et al.*[10] These authors have identified this $CO(A \rightarrow X)$ emission for $\lambda > 165$ nm ($v'' = 3\text{–}6$).

2. Continuum

The emission underlying the structured CO emission (Fig. 1) is similar to that observed previously in the ArF-laser photolyses of a number of chlorinated compounds.[3,4] From the varying number of Cl atoms in the molecules studied one can safely conclude that this seemingly continuous VUV emission is due to the formation of excited Cl_2 molecules. The most likely state producing this emission is $Cl_2(1\,^1\Sigma_u^+)$, which has been extensively studied by synchrotron radiation.[11,17] Probably the interference pattern recently observed for this bound-free $Cl_2(1\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+)$ emission close to the long wavelength limit[11] is smeared out in our spectra since, contrary to the synchrotron study, a number of vibrational states might be generated in the present photodissociation experiment. The emission at about 199 nm most likely represents the long wavelength limit of the

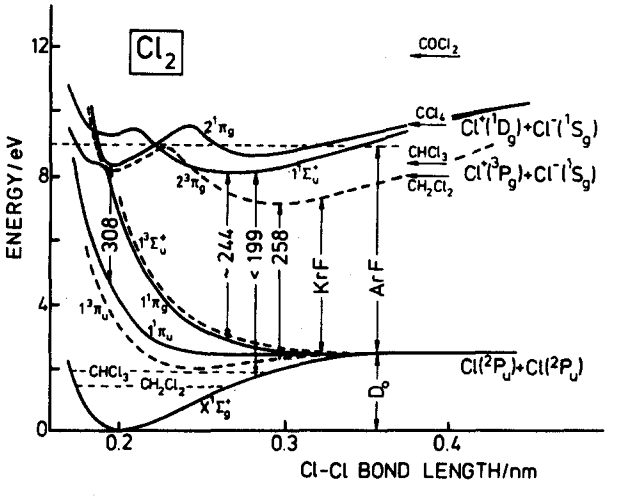

FIG. 4. Cl_2 potential energy curves relevant to the present study and according to Ref. 5. The observed emissions are indicated by arrows and wavelength in nm. The energy available from two ArF-laser photons for excitation of Cl_2 is shown by horizontal arrows for $COCl_2$, CCl_4, $CHCl_3$, and CH_2Cl_2. The sum of the dissociation energy and ArF laser photon energy is given by the horizontal dashed line at 8.9 eV. The energy excess in the photolyses of $CHCl_3$ and CH_2Cl_2 by one ArF-laser photon is indicated by the two dashed lines in the ground state potential curve.

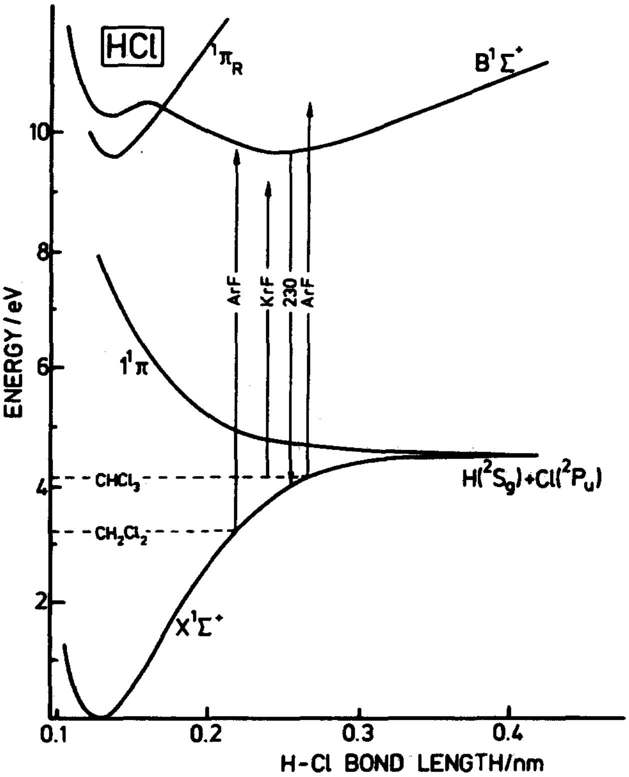

FIG. 5. HCl potential energy curves relevant to the present study and according to Refs. 21 and 22. The meaning of the additional arrows and dashed lines is as in Fig. 5.

TABLE II. Comparison of the structured VUV emission in the photolysis of $COCl_2$ with wavelength positions and Franck–Condon factors (FCF) for the $CO(A\,^1\Pi, v' = 1 \rightarrow X\,^1\Sigma^+, v'')$ emissions.

λ_{exp} (nm)	λ_{tab} (nm)[a]	v',v''	FCF[b]	Intensity $\times\lambda^3$ [c]
151	150.97	1,0	0.216	0.17
156	156.01	1,1	0.155	0.14
~162	161.95	1,2	0.003	<0.05
167	166.97	1,3	0.076	0.08
173	172.93	1,4	0.193	0.10
179.5	179.24	1,5	0.186	0.13
~186	185.94	1,6	0.108	<0.05

[a] The tabulated wavelengths are taken from Ref. 28.

[b] The Franck–Condon factors are taken from Ref. 29.

[c] The measured intensities were neither corrected for the spectral sensitivity of the optical detection nor for absorption by the parent molecule $COCl_2$, but they were corrected for their wavelength position.

VUV emission[10,11] and hence, the minimum energy separation of the $1\,^1\Sigma_u^+$ and $X\,^1\Sigma_g^+$ potential curves. This emission at $\lambda \approx 199$ nm appears to be present in the photolysis experiments by Okabe *et al.*,[30] the ArF-laser photolyses of CCl_4 by Tiee *et al.*,[2] and $COCl_2$ by Wilson *et al.*[10] The latter authors propose the transitions $Cl_2(1\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ or $1\,^1\Pi_g)$ to be responsible for the 199 nm emission, which, in their Fig. 1,[10] is indicated by the transition to the repulsive $Cl_2(^1\Pi_g)$ state. The calculated potential curves,[5] on the other hand, imply that the $Cl_2(1\,^1\Sigma_u^+ \rightarrow 1\,^1\Pi_g)$ transition generates light at longer wavelengths.

B. UV emission

1. 258 nm and below

The 258 nm emission can be assigned to the transition from the lowest bound triplet $2\,^3\Pi_g$ state to the weakly bound $1\,^3\Pi_u$ state which generates the Cl_2 laser emission.[5,10,30] When gases are added to the CCl_4 or $COCl_2$ photolysis system, this emission becomes the dominant fluorescence in the UV region (Fig. 2). Obviously, the $2\,^3\Pi_g$ state, which is the lowest bound state above the dissociation energy, is fed by other more energetic states.

The emissions observed at wavelengths shorter than the 258 nm continuum are partly generated from states above the lowest bound triplet state since they are efficiently quenched. These emissions have been recently attributed to the triplet transition from $2\,^3\Pi_u$ to the dissociative $1\,^3\Pi_g$ state.[10] They could additionally originate from the $1\,^1\Sigma_u^+$ state which might emit to the repulsive $1\,^1\Pi_g$ state. At any rate, Okabe *et al.*[30] locate the emitting state at an excitation energy between 7.33 and 8.93 eV.

2. 306 nm

The 306 nm emission has also been observed in the VUV photolysis of $COCl_2$[30] and in the ArF-laser photolysis of CCl_4[2] but not in the previous ArF-laser photolysis of $COCl_2$.[10] We believe that this emission is due to the transition from the inner well of the $2\,^1\Pi_g$ state to the repulsive $1\,^1\Pi_u$ state. Okabe *et al.*[30] have the emitting state reported to be located at 7.93 ± 0.03 eV, which is slightly lower than but close to the calculated inner minimum of the $2\,^1\Pi_g$ potential curve.[5] Furthermore, Spence *et al.*[16] have determined the $2\,^1\Pi_g$ state to lie at 7.939 eV while the experimental vertical excitation energy for the repulsive $1\,^1\Pi_u$ is 3.76[15] or ≈ 3.78 eV[1] (again slightly lower than the calculated value[5]). Since the inner well of $2\,^1\Pi_g$ has a bond length slightly smaller than the ground state, the energy difference between $2\,^1\Pi_g$ and $1\,^1\Pi_u$ matches the wavelength of the continuum at 306 nm. Considering all calculated potential curves,[5] no other allowed transition from an excited state near 8 eV can be found to emit close to 306 nm. The accompanying (almost) regularly spaced emission maxima at wavelengths down to 270 nm might be caused by the interference pattern which can be observed for bound-free transitions.

Recently, Fournier *et al.*[31] have observed 309.8 nm emission in the irradiation of Cl_2 in argon matrices. They find the threshold for excitation to be at 150 nm (8.266 eV) and assign the fluorescence to the transition from the outer minimum of the $2\,^3\Pi_g$ state to the repulsive $1\,^3\Sigma_u^+$ state, which correlates with ground state atoms. The $Cl_2(2\,^3\Pi_g \rightarrow 1\,^3\Pi_u)$ transition apparently is not observed in their experiment although it is usually detected in the gas phase. To generate $Cl_2(2\,^3\Pi_g)$ molecules in the outer minimum of the potential curve they propose the absorption step $Cl_2(2\,^3\Pi_g, v' = 4 \leftarrow X\,^1\Sigma_g^+)$ into the inner well of $2\,^3\Pi_g$ followed by tunneling into the outer well and relaxation. Regarding the complexity of this formation process, the unusual red-shift of the observed emission and the lack of $Cl_2(2\,^3\Pi_g \rightarrow 1\,^3\Pi_u)$ emission,[31] we suggest that the $Cl_2(2\,^1\Pi_g \rightarrow 1\,^1\Pi_u)$ transition be considered. Although direct excitation of $Cl_2(2\,^1\Pi_g)$ by absorption is not possible in the gas phase because of the *g–u* selection rule, this rule might be violated in the matrix as the authors state.[31]

3. 230 nm

When the molecule contains at least one H atom, as in $CHCl_3$ or CH_2Cl_2, extra emission can be observed having a maximum in intensity at 230 nm (Fig. 3). We attribute this emission to the $HCl(B\,^1\Sigma^+ \rightarrow X\,^1\Sigma^+)$ transition originating from the outer well of the upper ionic state. HCl potential curves have been recently calculated (Fig. 5).[21] They show a double well for $B\,^1\Sigma^+$ similar to that of the $Cl_2(1\,^1\Sigma_u^+)$ state (Fig. 4).[5,21] Subsequently, more extensive calculations resulted in lowering the minimum of the outer well to $T_e = 9.67$ eV[22] at about 2.5 Å bond length. These values are in good agreement with those determined by emission from a discharge ($T_0 = 9.45$ eV, $r_e = 2.43$ Å).[18] In that work, emission was photographed having a sharp long wavelength cutoff at 237.5 nm in agreement with the present work. Similar emission has also been observed by exciting HCl using VUV synchrotron radiation.[19]

It should be noted from the potential curves that the HCl transition to the dissociative $1\,^1\Pi$ state is predicted to generate a continuum at about 255 nm which, in fact, has been observed before in a discharge.[18] Emission at this wavelength is also observed in Fig. 3 for $CHCl_3$. From the present work, however, it cannot be decided whether this emission is due to the $HCl(B\,^1\Sigma^+ \rightarrow 1\,^1\Pi)$ or to the $Cl_2(2\,^3\Pi_g \rightarrow 1\,^3\Pi_u)$ transition.

4. 222 nm

It has been shown previously that KrCl emission at 222 nm can be formed by the reaction of excited Cl_2 with Kr[6]:

$$Cl_2^* + Kr \rightarrow KrCl^* + Cl. \qquad (7)$$

KrCl emission can therefore be indicative for the presence of excited Cl_2^* molecules. Emission from $KrCl^*$ has also been observed in the previous ArF-laser study of $COCl_2$.[10] The reason that KrCl emission is observed in the present study for $COCl_2$, CCl_4, and $CHCl_3$, but not for CH_2Cl_2 will be explained in the following discussion by the energetics of the photodissociation process. (ArCl emission at 185 nm has not been detected in any case.)

C. Mechanisms of formation

In the ArF-excimer laser photolysis using the unfocused beam, one has to distinguish between two different mechanisms for the formation of fragments by absorption of two or more photons.[23] The first of these is sequential absorption of two photons by the parent molecule via a resonant (possibly dissociative) state. This absorption generates "superexcited" parent molecules, which then decay to yield the observed fragments. In the second mechanism, the first absorption step forms intermediates (possibly in excited, quenchable states) which subsequently absorb the second laser photon to form the fragments of interest either directly or by photodissociation. In the following we will discuss the results we obtained for the one-ArF-laser two-photon process and ArF + ArF-laser and ArF + KrF-laser experiments which clearly demonstrate that, in all cases, the second mechanism is the correct choice.

1. Two-photon ArF and ArF + ArF

In spite of their previous speculation on the mechanism, Tiee *et al.*[2] do not clearly decide in favor of one of the two formation possibilities in the ArF-laser photolysis of CCl_4. In the previous ArF-laser photolysis of $COCl_2$, it has been recognized that a vibrationally excited intermediate, $CO(X,v''=7)$, is formed since its transition to the excited $CO(A,v'=1)$ state is in resonance with ArF-laser light. This explains the single excitation of the $v'=1$ state.[4,10] On the other hand, the first mechanism has been preferred to explain the formation of the excited Cl_2.[4,10] In particular, Wilson *et al.* excluded Cl_2 as an intermediate, since it was believed to be transparent to ArF-laser light even for the highest vibrational excitation in the ground state.[10] As will be shown below, we do not agree with this reasoning.

Since the present preliminary results of the experiments with two delayed lasers in pump and probe arrangement show that the observed Cl_2 and HCl emissions are in all cases due to secondary absorption of primary intermediates, our task will now be to identify the appropriate fragments from the first photolysis step. It is known[25] that halogenated methanes give rise to one halogen atom in the near ultraviolet by breaking the weakest halogen bond. In the VUV region the rupture of the two weakest bonds occurs concurrently. Three bond scissions are rare events. Similarly, for $COCl_2$, the formation of two Cl atoms has been observed in the near-UV photolysis.[25] To our knowledge, no conclusive evidence has been provided for the production of Cl_2 or HCl at around 193 nm. In the following we will show for this wavelength that Cl_2 is formed in the photolyses of $COCl_2$, CCl_4, $CHCl_3$, and CH_2Cl_2 and that HCl is generated in the photolyses of $CHCl_3$ and CH_2Cl_2, most likely with low quantum yields.

The two ArF-laser photons which generate the electronically excited Cl_2 and HCl molecules provide a total energy of 12.83 eV. In the cases of Cl_2 and HCl emissions, the minimum observed electronic excitation energies are about 7.2 $[Cl_2(2\,^3\Pi_g)]$ and 9.5 eV $[HCl(B)]$ which leaves less than 5.6 and 3.3 eV for the respective dissociation processes yielding Cl_2 and HCl. With the known heats of formation[25–27] and this restriction, one can easily calculate that there are no dissociation processes energetically possible other than those generating Cl_2 and HCl directly together with the appropriate remainder of the parent molecule. Any other process would require three fragments to be formed and hence to consume much more energy than is available from two 193 nm photons. Furthermore, the high electronic excitation of more than 7.2 and 9.5 eV in the Cl_2 and HCl photoproducts cannot stem from the absorption of the second ArF laser photon (6.415 eV) alone. We therefore have to conclude that the second absorption step excites internally hot Cl_2 and HCl molecules which must be formed by the absorption of the first photon. Since the emission intensities observed in the present work are weak, either the quantum yield for the production of the absorbing fragments or the absorption cross sections are small.

The results of more detailed energy considerations of the photolysis processes are indicated in Table I and Figs. 4 and 5 with regard to the formation of the excited Cl_2 and HCl. In Fig. 4 the position of the highest energetically possible Cl_2 excitations (Table I) are shown by horizontal arrows. In addition, the dashed line at 8.9 eV represents the energy reached by the sum of the dissociation energy of Cl_2, $D_0 = 2.48$ eV and the energy of the ArF-laser light, 6.415 eV. It should be noted that no emissions were observed from excitation above this energy, in spite of the fact that conservation of energy allows this for $COCl_2$ and CCl_4. In fact, the shortest wavelengths detected in the VUV emission spectra are 142 ± 3 nm for CCl_4 [3] and 141 ± 2 nm for $COCl_2$ which are in excellent agreement with the limit of 8.9 eV. We take this as further evidence that excited, bound Cl_2 molecules which are energetically located below the dissociation limit are the intermediates absorbing the second ArF-laser photon.

The amount of excitation of these Cl_2 molecules can be easily estimated from the highest excitation energies observed and the known enthalpies of formation[25–27] (see Table I). As discussed above for $COCl_2$ and CCl_4, Cl_2 molecules with energies up to the dissociation limit participate in the second absorption step. Since in $CHCl_3$ and CH_2Cl_2 molecules the bonds are stronger, the first absorption process can yield Cl_2 molecules with excitations only up to the two dashed horizontal lines indicated within the ground state potential curve. In contrast to the previous conjecture,[10] we note that the calculated potential curves[5] imply excitation from these Cl_2 which, at the position of their outer turning points, can lead to the observed emissions. It should be noted that according to the calculated data of Table I the available energy for CH_2Cl_2 is slightly short of the excitation energy of $Cl_2(1\,^1\Sigma_u^+)$ (8.06 eV).[5] This can, however, be due to the combined uncertainties for the dissociation energy of CH_2Cl_2 (± 0.06 eV) and the calculated energy of $Cl_2(1\,^1\Sigma_u^+)$ (± 0.1 to 0.2 eV). On the other hand, the VUV emission intensity observed for CH_2Cl_2 is extremely small and its generation by impurities or by contamination of the photolysis vessel cannot be completely excluded.

Figure 5 demonstrates that the formation of electronically excited $HCl(B\,^1\Sigma^+)$ occurs similarly. Here, vibrationally excited $HCl(X)$ molecules are necessary to provide part of the energy for exciting $HCl(B)$ in the second absorption step. The corresponding maximum vibrational excitations of $HCl(X)$ (see Table I) are indicated by the two horizontal lines in Fig. 5 for the photolyses of both $CHCl_3$ and CH_2Cl_2. In the case of CH_2Cl_2, the energy available for the excitation of HCl appears to be smaller than the calculated energy of the $B\,^1\Sigma^+$. A possible explanation for this will be given in the next section.

One can see in Fig. 5 and Fig. 10 of Ref. 21 that the $HCl(^1\Pi)$ state, the inner minimum of $HCl(B\,^1\Sigma^+)$ and some other states also are within the reach of the energy of the second 193 nm photon. The lowest fluorescent state generated by vertical excitation of $HCl(X)$ is $(B\,^1\Sigma^+, v' = 8)$ at 10.25 eV.[20] All lower lying states are heavily predissociated.[20] We did not observe emission in the respective wavelength range at 121.1 nm and below, probably because the fluorescence yield is small (< 0.04)[20] and the detection sensitivity of the present system is very low at these wavelengths.

Obviously for the HCl intermediates formed in the 193 nm photolysis, only the singlet ground state is energetically accessible (Fig. 5), which in turn undergoes an allowed transition to the $HCl(B)$ state by absorbing a second ArF-laser photon. The remaining fragments, CCl_2 in reaction (4) and CHCl in reaction (6) are also generated in their singlet ground states if spin is conserved in the first photolysis step. The corresponding situation can be more complex in some cases for the Cl_2 intermediate. The CH_2 radical generated from CH_2Cl_2 by reaction (5) possesses a triplet ground state. With spin conservation, the other fragment Cl_2 ought to be produced in a triplet state but the available energy is insufficient to excite the lowest Cl_2 triplet states at about 2.1 eV (see Table I). The missing triplet emission at 254 nm and the extremely weak singlet emission might be indicative for the spin forbidden process. Furthermore, it should be noted for the formation of $Cl_2(1\,^1\Sigma_u^+)$ that the CH_2 radicals cannot be generated in their lowest singlet state, 0.392 eV above the ground state[32] because the available energy does not permit this.

Providing spin conservation is obeyed and considering the available energies and the singlet–triplet splittings of the photolysis fragments,[1,33] both triplet and singlet intermediates can be generated in the ArF-laser photolysis of $CHCl_3$ and CCl_4. Because of the large singlet–triplet splitting of CO,[1] only singlet fragments should be allowed for $COCl_2$ in reaction (1). It should be cautioned, however, not to stress the spin conservation rule too much since the low fluorescence intensities are not necessarily in support of it.

Subsequent, allowed transitions in the second absorption step can populate all observed Cl_2 states except $Cl_2(2\,^1\Pi_g)$. This state cannot be reached from the $Cl_2(X\,^1\Sigma_g^+)$ ground state because of the g–u selection rule, which usually is strict. Its excitation from the $(1\,^3\Pi_u)$ state, on the other hand, only violates spin conservation, which may be less rigorously obeyed for the heavy Cl_2 molecule. The detailed understanding of this process requires further work.

The KrCl* emission is an interesting monitor of the energy of reacting Cl_2^* since at least 8.06 eV are required to form excited KrCl* in reaction (7). Thus, CH_2Cl_2 cannot yield this emission [see reaction (5) of Table I] in agreement with the present results and the extremely weak VUV emission intensity. On the other hand, the occurrence of this emission in the photolysis of $CHCl_3$ demonstrates that (almost) all excess energy appears in the observed Cl_2^* fragments [reaction (3)]. In the photolyses of CCl_4 and $COCl_2$, the excess energies are much larger than 8.06 eV and such a detailed conclusion cannot be drawn. For the formation of ArCl* emission, the excitation energy of Cl_2^* has to be at least 9.2 eV. As stated above, the excitation energy of Cl_2^* most likely does not exceed 8.9 eV for all molecules studied here. This inference is in agreement with the lack of ArCl* fluorescence at 185 nm.

2. ArF + KrF

The energy of a KrF-laser photon (5.000 eV) is significantly less than that of an ArF-laser photon (6.415 eV). Therefore, the number of states capable of being reached by the second KrF-laser photon is reduced to $Cl_2(2\,^3\Pi_g)$ and some other triplet states[12,13] close to the $Cl_2(2\,^3\Pi_g)$ state. This can be easily seen for Cl_2 fragments being formed by the first 193 nm photon and having an excitation energy of slightly less than D_0. Then the Cl_2 excitation can be at most 7.48 eV, which is well above the excitation energy of $Cl_2(2\,^3\Pi_g)$ (7.185)[14] but below the lowest excited bound singlet state. In the ArF-laser photolyses of CCl_4 and $COCl_2$ which form these highly excited Cl_2 molecules, the detection of triplet emission at 254 nm therefore is of no surprise. But for $CHCl_3$, the data of Table I suggest that the total energy might be insufficient for generating the 254 nm emission. The fact that triplet emission still is observed for $CHCl_3$ will be explained in the next section.

It is evident from Fig. 5 that no excited bound state of HCl can be reached in the ArF + KrF-laser experiments. From the above discussion it is furthermore clear that two KrF-laser photons have insufficient energy for the formation of highly excited bound Cl_2 and HCl states.

D. Enthalpy of formation of CHCl

In this section we will discuss two peculiarities already mentioned: The apparent lack of energy (1) to excite $HCl(B\,^1\Sigma^+)$ in the case of the two ArF-laser photon photolysis of CH_2Cl_2 and (2) to form $Cl_2(2\,^3\Pi_g)$ and /or higher triplet states in the case of the mixed ArF + KrF-laser photolysis of $CHCl_3$. Both processes [reactions (3) and (6)] have the photofragment CHCl in common. Of all the values for the enthalpies of formation used in the present work, that for CHCl($\Delta H^0_{f0} = 334 \pm 45$ kJ mol^{-1} [27]) is the least accurately known. In fact, the absolute uncertainty of this value is about 30 times greater than the combined uncertainties of the other species involved in the two relevant photodissociation processes. From the energetics of the photodissociation processes, an upper limit of the enthalpy of formation can be estimated. Most appropriate for this purpose appears to be the formation of $Cl_2(2\,^3\Pi_g)$ in the ArF + KrF-laser photolysis of $CHCl_3$ since (a) the electronic excitation energy of $Cl_2(2\,^3\Pi_g)$ is accurately known[14] and (b) vertical excitation of the potential minimum appears to be possible for the primary Cl_2 photodissociation products. Both presuppositions are not fulfilled that well for the other process forming $HCl(B\,^1\Sigma^+)$ (see Fig. 5). With the use of Eq. (8):

$$\Delta H^0_{f0}(\mathrm{CHCl}) = E(\mathrm{ArF}) + E(\mathrm{KrF}) + 3/2RT + \Delta H^0_{f0}(\mathrm{CHCl_3}) - \Delta H^0_{f0}(\mathrm{Cl_2}) - \Delta E(\mathrm{Cl_2^*}) \quad (8)$$

we calculated ΔH^0_{f0}(CHCl) to be <314 kJ mol^{-1}. An upper limit is given because we cannot exclude formation of internal energy in the fragments and excitation of triplet states higher then $Cl_2(2\,^3\Pi_g)$. In this equation, $\Delta H^0_{f0}(X)$ is the enthalpy of formation of species X at 0 K and 1 atm, E(ArF) and E(KrF) are the energies of ArF and KrF-laser photons and $\Delta E(Cl_2^*)$ is the excitation energy of Cl_2.

In a previous work[3] the short wavelength cutoff for the VUV emission was observed to be 143 ± 3 nm in the two-photon ArF-laser photolysis of $CHCl_3$. Replacing (KrF) by E(ArF) and taking the energy for this wavelength into account for $\Delta E(Cl_2^*)$, we obtain a value of (307 ± 17) kJ mol^{-1} for ΔH^0_{f0}(CHCl). Also, this value will be an upper limit if not all the excess energy appears in the fluorescent Cl_2 and if the excited Cl_2 does not emit to the lowest levels of the ground state. With this new value for ΔH^0_{f0} (CHCl) the energy available in reaction (6) for the two-ArF-laser-photon generation of HCl(B) is 9.68 eV (instead of 9.40 eV). This energy is sufficient to excite HCl ($B\,^1\Sigma^+$) in the case of CH_2Cl_2 [see point (1) above].

V. CONCLUSION

This paper presents a report on a study of the fluorescence emissions in the ArF-laser photolyses of chlorinated methanes and $COCl_2$ using an unfocused laser beam. These emissions were produced by absorption of two photons and were identified to originate from different (singlet and triplet) states of highly excited Cl_2 for the photolyses of $COCl_2$, CCl_4, $CHCl_3$, and CH_2Cl_2 and from HCl(B) for $CHCl_3$ and CH_2Cl_2. Pump and probe experiments with two ArF and ArF + KrF lasers established the existence of intermediates in each case. These intermediates were recognized to be Cl_2 excited below the dissociation limit and vibrationally excited HCl molecules in their electronic ground state. Excitation energies up to the dissociation limit were observed for Cl_2 in the photolyses of $COCl_2$ and CCl_4. The formation of excited Cl_2 and HCl in the first absorption step most likely are minor photolysis processes and hence are of secondary importance for stratospheric photochemical processes which occur at around 200 nm. The experimental technique applied in this work presents a very sensitive tool to monitor minor photolysis products with small excitation energies.[23] It further allows one to prepare molecules in the outer minima of double-minimum potential curves by vertical excitation from the outer turning points of the hot molecules at long bond distances. Energy considerations lower the reported value of the heat of formation of CHCl to less than 307 ± 17 kJ mol^{-1}.

ACKNOWLEDGMENTS

The authors thank Dr. D. Haaks and Professor S. D. Peyerimhoff for valuable discussions, Dr. L. C. Lee for providing us preprints of his work, and the Deutsche Forschungsgemeinschaft (SFB 42) and Fonds der Chemischen Industrie for financial support.

[1] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
[2] J. J. Tiee, F. B. Wampler, and W. W. Rice, J. Chem. Phys. **72**, 2925 (1980).
[3] H. K. Haak and F. Stuhl, Chem. Phys. Lett. **68**, 399 (1979).
[4] H. K. Haak, Dissertation, Ruhr-Universität Bochum, 1982.
[5] S. D. Peyerimhoff and R. J. Buenker, Chem. Phys. **57**, 279 (1981).
[6] M. C. Castex, J. Le Calvé, D. Haaks, B. Jordan, and G. Zimmerer, Chem. Phys. Lett. **70**, 106 (1980).
[7] J. Le Calvé, M. C. Castex, D. Haaks, B. Jordan, and G. Zimmerer, Il Nuovo Cimento B **63**, 265 (1981).
[8] T. Ishiwata, I. Fujiwara, and I. Tanaka, Chem. Phys. Lett. **89**, 527 (1982).
[9] A. E. Douglas, Can. J. Phys. **59**, 835 (1981).
[10] M. W. Wilson, M. Rothschild, and C. K. Rhodes, J. Chem. Phys. **78**, 3779 (1983).
[11] T. Moeller, B. Jordan, P. Gürtler, G. Zimmerer, D. Haaks, J. Le Calvé, and M. C. Castex, Chem. Phys. **76**, 295 (1983).
[12] T. Ishiwata, I. Fujiwara, T. Shinzawa, and I. Tanaka, J. Chem. Phys. **79**, 4779 (1983).
[13] T. Ishiwata, T. Shinawa, T. Kusayanagi, and I. Tanaka, J. Chem. Phys. **82**, 1788 (1985).
[14] T. Shinzawa, A. Tokunaga, T. Ishiwata, and I. Tanaka, J. Chem. Phys. **83**, 5407 (1985).
[15] J. Jureta, S. Cvejanović, M. Kurepa, and D. Cvejanović, Z. Phys. Teil A **304**, 143 (1982).
[16] D. Spence, R. H. Huebner, H. Tanaka, M. A. Dillon, and R.-G. Wang, J. Chem. Phys. **80**, 2989 (1984).
[17] L. C. Lee, M. Suto, and K. Y. Tang (private communication).
[18] J. K. Jacques and R. F. Barrow, Proc. Phys. Soc. London **73**, 538 (1958).
[19] D. Haaks (private communication).
[20] J. B. Nee, M. Sato, and L. C. Lee (private communication).
[21] M. Bettendorff, S. D. Peyerimhoff, and R. J. Buenker, Chem. Phys. **66**, 261 (1982).
[22] S. D. Peyerimhoff (private communication).
[23] R. D. Kenner, F. Rohrer, and F. Stuhl, Chem. Phys. Lett. **116**, 374 (1985); R. D. Kenner, F. Rohrer, Th. Papenbrock, and F. Stuhl, J. Phys. Chem. **90**, 1294 (1986).
[24] H. K. Haak and F. Stuhl, J. Phys. Chem. **88**, 2201 (1984); K. Shibuya and F. Stuhl, Chem. Phys. **94**, 167 (1985); A. Hofzumahaus and F. Stuhl, J. Chem. Phys. **82**, 5519 (1985).
[25] H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978).
[26] D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **13**, 1259 (1984).
[27] D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., Natl. Bur. Stand. NSRDS-NBS No. 37 (U. S. GPO, Washington, D.C., 1970).

[28] P. H. Krupenie, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. No. 5 (U.S. GPO, Washington, D.C., 1966).
[29] R. W. Nicholls, J. Quant. Spectrosc. Radiat. Transfer 2, 433 (1962).
[30] H. Okabe, A. H. Laufer, and J. J. Ball, J. Chem. Phys. 55, 373 (1971).
[31] J. Fournier, F. Salama, and R. J. LeRoy, J. Phys. Chem. 89, 3530 (1985); F. Salama and J. Fournier, Chem. Phys. Lett. 120, 35 (1985).
[32] A. R. W. Mc Kellar, P. R. Bunker, T. J. Sears, K. M. Evenson, R. J. Saykally, and S. R. Langhoff, J. Chem. Phys. 79, 5251 (1983).
[33] C. W. Bauschlicher, Jr., H. F. Schaefer III, and P. S. Bagus, J. Am. Chem. Soc. 99, 7106 (1977).