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Vibrational energy and bimolecular reactions: Enhancement of the electron transfer derived product channels for quenching of $Xe({}^{3}P_{2})$ and $Kr({}^{3}P_{2})$ atoms by $CF_{n}CI_{4-n}$, $C_{2}F_{n}CI_{6-n}$, and $CF_{3}CFCICF_{2}CI$

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The yields of XeCl(*B*,*C*) and KrCl(*B*,*C*) from the reactions of Xe(${}^{3}P_{2}$) and Kr(${}^{3}P_{2}$) metastable atoms with chlorofluoromethanes and chlorofluoroethanes are enhanced by the addition of vibrational energy to the molecule. The reactions were studied in a fast flow reactor with He or Ar carrier gas; vibrational energy was added to the molecules by multiphoton absorption from a CO₂ laser pulse at fluences of 0.2–1.0 J cm⁻². The enhancement of the XeCl(*B*,*C*) or KrCl(*B*,*C*) product was observed by monitoring the *B*-*X* fluorescence intensity in real time following excitations by the CO₂ laser. Enhancement factors are reported for reactions with CF₂Cl₂, CFCl₃, CF₃CFCl₂, CF₂ClCF₂Cl, CF₂ClCFCl₂, and CF₃CFClCF₂Cl; survey experiments are presented to demonstrate enhancement of XeCl* and XeBr* from vibrationally excited CF₂BrCl and CF₃CH₂Br. The decay times of the XeCl(*B*) and KrCl(*B*) signals provide information about the relaxation rates of the vibrationally excited CF_nCl_{4-n} and C₂F_nCl_{6-n} molecules. In order to have a reliable reference, the total quenching rate constants and the branching fractions for XeCl(*B*,*C*) and KrCl(*B*,*C*) formation for 300 K conditions also were measured for most of the compounds; the branching fraction for XeCl* formation form CF₃CCl₃ is large for a polyatomic molecule.

INTRODUCTION

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The availability of infrared lasers was expected to permit demonstration of the enhanced reactivity of vibrationally excited molecules in bimolecular reactions. Indeed there are a few examples, mainly for the atom plus diatomic molecule class of reactions, for which vibrational energy enhances the rate of reaction or alters the dynamics of product formation.¹⁻⁷ However, frequently little effect upon reaction rates has been observed following specific vibrational excitation of reactants, especially for polyatomic systems, because of rapid vibrational energy relaxation and/or the small effect of vibrational energy upon the reaction rates.^{1,2,6,7} In a preliminary report,⁸ we showed that vibrational energy did alter the product distribution for reactive collisions of metastable $Xe({}^{3}P_{2})$ atoms with CF₃Cl, CF₂Cl₂, and CHF₂Cl. The prototype reactant was CF₂Cl₂; the two major exit channels for 300 K Boltzmann conditions are XeCl(B,C) formation and dissociative excitation transfer^{9,10}

$$CF_{2}Cl_{2} + Xe(6s^{3}P_{2}) \xrightarrow{\kappa_{1a}} XeCl(B,C) + CF_{2}Cl$$

$$\xrightarrow{k_{1b}} \rightarrow CF_{2}Cl_{2}^{*} + Xe, \qquad (1a)$$

$$CF_2Cl_2^* \rightarrow CF_2Cl + Cl, \qquad (1b)$$
$$\rightarrow CF_2 + 2Cl$$

The total quenching¹¹ rate constant, $k_{1a} + k_{1b}$, at 300 K is $1.9 \pm 0.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ with a branching fraction for XeCl(*B*,*C*) formation Γ_{XeCl^*} of only ~0.02.^{8,9} However, the addition of vibrational energy to CF₂Cl₂ with a pulsed CO₂ laser greatly enhanced XeCl(*B*,*C*) formation⁸

$$CF_2Cl_2 + mhv \to CF_2Cl_2^{\dagger}, \qquad (2)$$

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$$\operatorname{CF}_{2}\operatorname{Cl}_{2}^{\ddagger} + \operatorname{Xe}(6s^{3}P_{2}) \xrightarrow{k \ddagger_{a}} \operatorname{XeCl}(B,C) + \operatorname{CF}_{2}\operatorname{Cl}, \quad (3a)$$

$$\stackrel{k^{\dagger}_{b}}{\rightarrow} CF_{2}Cl_{2}^{*} + Xe. \qquad (3b)$$

Estimation of the fraction of the molecules interacting with the laser field for a fluence of $\sim 1 \text{ J cm}^{-2}$ suggested that Γ_{XeCl} for the vibrationally excited molecules could be as high as ~ 0.5 . The enhancement was associated with an increased value for k_{1a}^{\ddagger} at the expense of k_{1b}^{\ddagger} because the total quenching rate constant $(k_{1a} + k_{1b})$ for the cold molecules already is nearly at the gas kinetic limit, and it seems unlikely that $(k_{1a}^{\dagger} + k_{1b}^{\dagger})$ would increase significantly. The enhancement of the XeCl(B,C) product at the expense of the dissociative excitation-transfer channel for vibrationally excited molecules correlates with the energy and temperature dependence of the dissociative electron attachment cross section of CF_2Cl_2 , which is natural since the reaction mechanism for reaction (1a) involves the ion pair $V(Xe^+; CF_2Cl_2^-)$ intermediate potential. In the present work, new experimental evidence is provided to support our claim for the vibrational energy enhancement of Γ_{XeCl^*} from $Xe({}^{3}P_{2}; 8.3 \text{ eV})$ with $CF_{2}Cl_{2}$; the experiments include laser pumping in both the 925 and 1050 cm^{-1} absorption bands. Several additional members of this reaction class are reported and experiments were done in both He and Ar carrier gas. Specifically, enhancement of KrCl(B,C) formation from the reaction of $Kr(5s^3P_2, 10.5 \text{ eV})$ with $CF_2Cl_2^{\ddagger}$ and enhancement of both KrCl(B,C) and XeCl(B,C) formation from reactions with CFCl[‡], CF₃CFCl[‡], CF₂ClCF₂Cl[‡], and $CF_3CFClCF_2Cl^{\ddagger}$ have been studied in detail. The competition between XeCl(B) and XeBr(B) formation was studied

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with cold and excited CF_2ClBr . Improvement of the signal recording instrumentation has given better temporal definition of the XeCl(B) and KrCl(B) fluorescence signals and the relaxation rates of the vibrationally excited molecules are deduced from the XeCl* or KrCl* decay times. Quantitative correlation between the enhancement of Γ_{XeCl^*} or Γ_{KrCl^*} and the amount of vibrational energy in the reagent molecule is prevented by our limited knowledge about the vibrational distributions resulting from multiphoton energy absorption from the CO₂-laser field. A few experiments were done with CF_3CH_2Br and $Xe({}^{3}P_2)$, because the energy absorption by CF₃CH₂Br has been characterized^{12(a)}; however, enhancement of XeBr(B,C) formation was small for this molecule. In general, we expect bimodal vibrational distributions for the modest fluence used in these experiments because of rotational bottlenecking in the lower vibrational states, i.e., a significant fraction of the molecules do not interact with the laser field. The fraction that does interact with the laser field will be larger for the chlorofluoroethanes than for the chlorofluoromethanes.¹²

The experiments consist of observing the XeCl(*B*-X), KrCl(*B*-X), or XeBr(*B*-X) fluorescence form a flow reactor containing Xe(${}^{3}P_{2}$) or Kr(${}^{3}P_{2}$) atoms with the added reagent before and after a CO₂-laser pulse is passed through the observation zone. In the absence of the laser pulse, the kinetics are in the steady-state limit with fluorescence intensity equal to the XeCl(*B*,*C*) formation rate. The collisionally coupled XeCl(*B* and *C*) states can be approximately treated as a single state with an effective radiative decay constant τ_{eff} :

$$I(\text{XeCl}^*) = \tau_{\text{eff}}^{-1}[\text{XeCl}^*] = k_{1a}[\text{Xe}({}^{3}P_2)][\text{RCl}] . (4)$$

For our operating conditions, $[Xe({}^{3}P_{2})]$ is $\sim 3 \times 10^{10}$ atom cm⁻³ and [RCl] is $0.5-1.0 \times 10^{12}$ molecule cm³ for 0.5-3.0 Torr of Ar or He carrier gas. The $[Xe({}^{3}P_{2})]$ decays along the length of the flow reactor with a pseudo-first-order rate law. When the unfocused laser beam passes through the cell, a fraction of the RCl molecules are excited to higher vibrational levels. These vibrationally excited molecules are collectively denoted as RCl[‡] in Eq. (2). After the laser pulse, the total $I(XeCl^*)$ is given by Eq. (5)

$$I(XeCl^*) = [Xe({}^{3}P_2)](k_{1a}[RCl-RCl^{\ddagger}] + k_{1a}^{\ddagger}[RCl^{\ddagger}]).$$
(5)

Since $[Xe({}^{3}P_{2})]$ is unchanged by the laser pulse, the enhanced $I(XeCl^*)$ signal is proportional to the product $k_{1a}^{\dagger}(\mathbf{RCl}^{\dagger})$. The laser pulse is short compared to the residence time of the gas in the observation zone, and the decay rate of $I(XeCl^*)$ follows the vibrational relaxation of the [RCl[‡]] from collisions with the He or Ar carrier gas. It is probable that k_{1a}^{\dagger} depends upon the level of vibrational excitation and the $k_{1a}^{\ddagger}[RCl^{\ddagger}]$ product actually should be а sum over vibrational energy states $\Sigma_{E_v} k_{1a}^{\ddagger}(E_v) [\text{RCl}^{\ddagger}(E_v)]$. In this study we have not identified these individual terms, although the dependence of $I(XeCl^*)$ upon the laser fluence, the structure of RCl[‡], and the decay rates of RCl[‡] molecules provide some clues. The main goal of the present study was to enlarge the number of reagents exhibiting vibrational enhanced XeCl* and KrCl* formation and to refine the experimental technique, rather than to characterize the energy absorption in the multiphoton absorption event. Since XeCl* and KrCl* formation from reaction of Xe(${}^{3}P_{2}$) and Kr(${}^{3}P_{2}$) with the chlorofluorethanes and CF₃CFClCF₂Cl has not been studied before, the quenching rate constants and the rate constants for XeCl* and KrCl* formation for several of these molecules at 300 K were measured for reference.

This paper has the following organization: The apparatus, with emphasis on the improvements relative to the first report,⁸ is described in the Experimental section. Next, the 300 K quenching rate constants and branching fraction measurements for XeCl(*B*,*C*) and KrCl(*B*,*C*) formation at 300 K are summarized. The characteristics of the Kr(³P₂) and Xe(³P₂) metastable atom source in He carrier is described and compared with the more conventional Ar carrier in this section.¹³ The third section describes the diagnostic tests used to ascertain that the CO₂-laser enhanced XeCl^{*} and KrCl^{*} yields truly arise from vibrationally excited molecules. Next, the vibrational energy enhancement factors for XeCl^{*} and KrCl^{*}, $F_{\phi}^{XeCl^*}$ and $F_{\phi}^{KrCl^*}$, and the time profiles for the enhancements are presented and analyzed. The paper is concluded by a short Discussion section.

EXPERIMENTAL METHODS

The metastable atoms $Kr({}^{3}P_{2})$ or $Xe({}^{3}P_{2})$ were generated in a low current dc discharge (\sim 280 V and 1 mA) in He or Ar buffer gas.¹³ The cylindrical electrodes (20 mm long and 9 mm diameter) were made from tantalum foil and placed 22 mm apart. For most experiments Kr or Xe were added to the carrier gas at a constant flow rate of 25 μ mol s⁻¹. A 110 ℓ s⁻¹ Pfeiffer-Balzers pump with booster gave 1-10 Torr pressure for a carrier gas flow of 1-10 mmol s^{-1} . The Kr and Xe, which were supplied by Spectra Gases Inc. with a specified purity of 99.99%, were used directly from the tank. The Ar and He (99.99% Knoll Welding) was passed through molecular sieve filled traps cooled by dry ice/acetone and liquid nitrogen baths. The reagent gases were obtained from SCM Specialty Chemicals Inc., purified by vacuum trap to trap distillation and stored in glass reservoirs. The metastable Xe* or Kr* atom concentration in He carrier was about three times larger than in Ar carrier for the same total pressure. The reagents were added to the reactor by a four-jet injector arrangement to obtain uniform premixing before the gas flow reached the irradiation zone.

The reaction zone was irradiated with the unfocused output of a 0.5 Hz Lumonics TEA CO₂ laser through the NaCl windows (see Fig. 1). The laser fluence 0.2–1.5 J cm⁻² was below the multiphoton unimolecular dissociation threshold for the reagent molecules. The laser wavelength was tuned to the absorption bands associated with the C-F or C-Cl stretch frequencies in the 1080–1050 or 900– 950 cm⁻¹ regions (see Fig. 2). The rise time of the laser pulse was 100 ns with a pulse length of 1–2 μ s, depending on the laser gas (He/CO₂/N₂) composition. A small fraction of the laser beam was directed to a photon drag detector (RO-FIN LTD) for recording the pulse shape. A second small fraction was directed to a CO₂-laser spectrum analyzer for laser tuning. The main part of the beam passed through an



FIG. 1. Schematic representation of the experimental apparatus used to observe the vibrational enhancement factors for XeCl(B,C) and KrCl(B,C) formation. (IF—interference filter, PDD—photon drag detector, G.S.S.S.—galvanic separator and surge suppressor.) The flow reactor was of standard design (Ref. (13) with the discharge source attached to the top of the reactor. The reagent inlet was a four-jet arrangement designed to obtain planar mixing.

aperture to obtain a 19.5 mm diameter (3 cm^2) beam of nearly constant fluence and directed without focusing to the flow reactor. The laser energy was measured using a Scientech pyroelectric calorimeter.

Characteristic XeCl* and KrCl* emission spectra from the 300 K reactions of Xe(${}^{3}P_{2}$) or Kr(${}^{3}P_{2}$) with several molecules are shown in Figs. 3(a) and 3(b). These spectra were recorded using a 0.3 m McPherson monochromator with 1200 grooves/mm grating, Hamamatsu 212 photomultiplier tube, and EGG-PAR photon counter. To monitor the vibrational energy enhanced XeCl* or KrCl* formation, the *B-X* emission was viewed either by the monochromator with wide (1 mm) slits or with narrow bandpass filters [Corion 313 ± 10 nm for XeCl(*B-X*) or Corion 222 ± 5 nm for KrCl(*B-X*)]. The scattered light arising from the laser beam striking the NaCl windows did not affect the XeCl(*B-X*) or KrCl(*B-X*) signals observed through the filters, unless the fluence was above 2 J cm⁻².

With reference to our former work,⁸ the detection system has been improved with respect to time resolution and signal averaging. As a result of numerous tests with the CO_2 laser in operation, the best recording of the weak XeCl* and KrCl* emission signals was obtained using current-to-voltage conversion (CVC) of the photomultiplier response with a homemade CVC circuit and transforming the output signal to 50 Ω impedance using a coaxial cable driver. The frequency bandwidth was $f_T = 8$ MHz and the amplification was about 10³ times larger than with direct termination of the photomuliplier tube signals to a 50 Ω resistor. The photomultiplier tube and CVC were powered by alkaline batteries to reduce electrical noise from the laser discharge. The output signal from the coaxial-cable driver was connected to the 50 Ω input of a digital storage scope LeCroy 9400. The second channel of the storage scope was connected to the output from the photon drag detector, which monitored the CO₂-laser pulse. The relation between the chemiluminescence signal and the laser pulse had good reproducibility with less than 50 ns jitter. The digital scope was triggered from the laser control unit using a homemade galvanic separator and electrical noise suppressor to avoid electromagnetic interference from the electrical discharge. To obtain adequate signal recording, 100, or more, laser pulses were necessary. The steady-state (i.e., without laser irradiation) XeCl* and KrCl* chemiluminescence signal viewed through a filter was typically $10^5 - 10^7$ counts s⁻¹, as measured with the photon counter. The CO₂-laser enhanced fluorescence gave signals which approached the photon bunch level. For such conditions, photon counters tend to become saturated. However, the CVC circuit did not have this disadvantage and correctly reproduced the XeCl* and KrCl* vibrationally enhanced signals.

The rather long time required to obtain a satisfactory waveform (because of the slow CO_2 -laser repetition rate) did not allow us to obtain XeCl(B-X) or KrCl(B-X) emission spectra from the vibrationally excited molecules using a monochromator to disperse the spectrum. Such experiments, which would be especially valuable for molecules prepared with known amounts of vibrational energy, are feasible with a higher repetition rate CO_2 laser or an optical multichannel analyzer (OMA) detector.

Infrared spectra at 0.5 cm^{-1} resolution of the reagents from a Digilab Fourier transform infrared (FTIR) spectrometer are shown in Fig. 2; the conventional Beer's Law absorption cross sections at the wavelengths used for the laser enhancement experiments are similar, as shown in Table I. However, these broadband cross sections provide only a rough measure of the laser absorption cross sections. Each molecule will have its own unique, pressure and fluence dependent, laser absorption cross section.^{8,12} Tests for multiphoton-induced unimolecular decomposition of reagents were done using IR absorption measurements in a 10 cm cell for an extended (100) number of pulses for a fluence of 1 J cm⁻².

The branching fractions for KrCl^{*} and XeCl^{*} formation and the total quenching rate constants for 300 K conditions $k_{1a} + k_{1b}$ were measured using techniques reported previously.^{9,11} Some improvements in the methods for measuring reagent flow rates using an automated apparatus and the total quenching rate constant data will be presented in a separate paper.¹⁴

EXPERIMENTAL RESULTS

Description of 300 K quenching results

The Kr(${}^{3}P_{2}$) and Xe(${}^{3}P_{2}$) metastable atom reactors with Ar carrier are well characterized and extensively used. 13 The Xe(${}^{3}P_{2}$) system works especially well, because the Ar(${}^{3}P_{0,2}$) metastable atoms formed in the discharge are rapidly converted to Xe(${}^{3}P_{2}$) atoms, even for low flows of Xe. The [Xe(${}^{3}P_{2}$)] is nearly as high as the [Ar(${}^{3}P_{0,2}$)] from a pure Ar discharge; the [Xe(${}^{3}P_{0}$)] is negligible. The Kr(${}^{3}P_{2}$) source in Ar carrier is less ideal and requires higher Kr flows because the quenching rate constants of Ar(${}^{3}P_{2}$) and Ar(${}^{3}P_{0}$) by Kr are much smaller than for Xe. In fact, the



FIG. 2. (a) Infrared absorption spectra for A--CF₂Cl₂ and B-CFCl₃. The 10 cm cell contained 5 Torr of each compound. The spectra are normalized to the strongest band for each molecule. $1-R(00^{\circ}1-02^{\circ}0); 2-P(00^{\circ}1-02^{\circ}0); 3-R(00^{\circ}1-10^{\circ}0); 4-P(00^{\circ}1-10^{\circ}0); 5-P(01^{1}1-11^{1}0)$ bands of the CO₂ laser. (b) Infrared absorption spectra for A--1,1-C₂F₂Cl₂, B--1,2-C₂F₄Cl₂, and C--1,2-C₃F₆Cl₂. The 10 cm cell contained 5 Torr of each compound. The spectra are normalized to the strongest band for each molecule.



FIG. 3. (a) The XeCl^{*} steady-state emission spectra from the reactions of $Xe({}^{3}P_{2})$ with A(Cl₂), B(CFCl₃), C(CF₃CCl₃), D(CF₂ClCFCl₂), and E(CF₃CFClCF₂Cl) at 300 K and 2 Torr of He. The spectra from CF₂ClCF₂Cl and CF₃CFCl₂ closely resemble that for CF₃CFClCFCl₂. The spectra have been corrected for the wavelength response of the detection system. (b) The KrCl^{*} emission spectra from the same reactions as specified in Fig. 3(a).

TABLE I. Broadband absorption cross sections at the laser wavelength.*

Molecule	Laser wavelength (cm ⁻¹)	$\frac{\text{Cross}}{\text{section } \sigma_0}$ 10^{-19} cm^{-2}
CF ₂ Cl ₂	R(38)-1089	8.9
CF ₂ Cl ₂	P(42)-923	10.2
CFCl ₃	R(38)-1089	5.4
CFCl ₃	R(8)-1070	5.4
CF ₂ ClBr	R(38)-1089	12.4
$1,1-C_2F_4Cl_2$	P(42)-923	5.8
$1,2-C_2F_4Cl_2$	P(42)-923	9.2
1,1,1-C ₂ Cl ₃ F ₃	P(48)-916 ^b	0.4
1,1,2-C ₂ Cl ₃ F ₃	P(14)-1052	8.8
1,2-C ₃ F ₆ Cl ₂	R(8) -1070	3.2
CF ₃ CH ₂ Br	R(26)-1082	6.2

^a These results are based upon absorption measurements at a single pressure (5 Torr) in a 10 cm length cell with a FTIR spectrometer at 0.5 cm⁻¹ resolution.

^b Sufficient laser power was not available for this line to accomplish multiphoton excitation. The other absorption bands are out of the range of our CO_2 laser. rate constant¹⁵ for $\operatorname{Ar}({}^{3}P_{0})$ is only $0.11 \times 10^{-12} \operatorname{cm}^{3} \operatorname{s}^{-1}$ and it is virtually impossible to remove all of the $\operatorname{Ar}({}^{3}P_{0})$ concentration. The $\operatorname{Kr}({}^{3}P_{2})$ and $\operatorname{Xe}({}^{3}P_{2})$ sources in Ar carrier can be operated at higher pressure than for $\operatorname{Ar}({}^{3}P_{2})$ because the three-body quenching rates are smaller; the low pressure limits are determined by the diffusion rates.

Study of the vibrational energy enhanced XeCl* and KrCl* formation in He, as well as Ar, carrier gas was desirable because the collisional release of the bottlenecks to infrared multiphoton absorption and the collisional deactivation of the vibrationally excited molecules differ for He and Ar. As noted in the Experimental section, the $Xe({}^{3}P_{2})$ and $Kr(^{3}P_{2})$ concentrations were about three times larger in He than in Ar for 2 Torr conditions. The absolute concentrations of $Xe({}^{3}P_{2})$ and $Kr({}^{3}P_{2})$ in 2 Torr of He were estimated to be $4 \pm 1 \times 10^{10}$ atom cm³ from atomic absorption measurements.¹⁴ The characteristic excited state distributions from reactions of CO and N2^{16,17} were used to test for the presence of $Xe({}^{3}P_{0})$ or $Kr({}^{3}P_{0})$ metastable atoms in He carrier. The concentrations of $Xe({}^{3}P_{0})$ was too low to measure; however, the $Kr({}^{3}P_{0})$ concentrations was about 10% of the $Kr(^{3}P_{2})$ concentration.¹⁷ For lower pressure conditions, the relative metastable atom concentrations in He and Ar were still about 3:1; however, the discharge in He tended to be somewhat unstable and required more Xe or Kr than at 2 Torr. For 2-3 Torr pressure, we normally used flows that gave $\sim -90\%$ of the maximum metastable atom concentration in order to conserve Xe and Kr. At lower pressures, higher Kr and Xe flows were required and the plateau region was less obvious. In He carrier, the excitation mechanism is thought to be collisions of electrons (and associated processes) with the Kr and Xe atoms that pass through the discharge zone, i.e., excitation of He is not involved in the generation of $Kr({}^{3}P_{2})$ or $Xe({}^{3}P_{2})$.

Since the reactions of $Kr({}^{3}P_{2})$ and $Xe({}^{3}P_{2})$ with 1,2- $C_2F_4Cl_2$, 1,1- $C_2F_4Cl_2$, 1,1,1- $C_2Cl_3F_3$, 1,1,2- $C_2Cl_3F_3$, and $1,2-C_3F_6Cl_2$ have not been fully characterized,¹⁰ these systems were investigated in order to assign k_{XeCl^*} and k_{KrCl^*} for 300 K Boltzmann conditions. Less extensive measurements with $Xe({}^{3}P_{2})$ also were done for $C_{2}H_{2}Cl_{4}$, $CF_3CCl = CCl_2$, CF_3CH_2Br , and CF_2ClBr . The XeCl(C-A) vs XeCl(B-X) intensity ratios were approximately 0.3 at 2 Torr of He for the different reagents (see Fig. 3). Because of their long radiative lifetime, more than one-half of the XeCl(C) molecules are collisionally transferred to the B state even at 2 Torr of He.¹⁸ Prior studies of the dependence of the C/B ratio on pressure suggest that the nascent C/Bratios would be in the range of ~ 0.8 .^{18(b)} The apparent low XeCl(C)/XeCl(B) ratios from C₂H₂Cl₄ and CF₃CClCCl₂ are unreliable because of very weak signal levels. The experimental spectra can be compared with previous simulations of the XeCl(B-X) spectra to estimate the average XeCl(B)vibrational energy.^{11,18} The fraction of the available energy released as XeCl(B) vibrational energy $\langle f_V(\text{XeCl}) \rangle$ is in the 0.2 range, except for CFCl₃ and CF₃CCl₃, for which $\langle f_V \rangle = 0.6$. The KrF(C-A)/KrF(B-X) ratios generally are higher than for XeCl* at the same pressure. This is probably a consequence of the somewhat shorter lifetime of KrCl(C) and the nascent C/B ratios for $KrCl^*$ are similar to



FIG. 4. The plot of I_{xeCl^*} vs added [RCl] for the same concentration of Xe(${}^{3}P_{2}$) in 3 Torr of He carrier gas. A—Cl₂, B—1,1,1-C₂Cl₃F₃, C—CCl₃F, D—1,2-C₃Cl₂F₆, and E—1,1,2-C₂Cl₃F₃.

those for the $Xe({}^{3}P_{2})$ reactions.

For reagent concentrations below $\sim 2 \times 10^{12}$ molecule cm³, the [Xe(³ P_2)] and [Kr(³ P_2)] in the observation zone are virtually constant and the XeCl(B-X) and KrCl(B-X) emission intensities are first order in [RCl]. Figure 4 shows a typical data set for adding several RCI to the same $[Xe({}^{3}P_{2})]$ in 2 Torr of He. According to Eq. (4), the relative slopes from these plots, adjusted for the total B_{-} X and C-A band intensities, correspond to the relative formation rate constants, which are defined as k_{XeCl}^{RCl} and $k_{\text{KrCl}}^{\text{RCl}}$. We selected Cl_2 as the reference reaction for the $Xe({}^{3}P_{2})$ reactions, because it had been previously studied in detail.⁹ The vibrational excitation of XeCl(B,C) from Cl₂ is extensive and the spectra is extended, but care was taken to include all of the B-X and C-A emission. The intensity vs concentration plots were linear up to $[RC1] \approx \langle 2 \times 10^{12}$ molecule cm^{-3} and the relative rate constants should be reliable to $\pm 20\%$. The results for Xe(³P₂), as measured in 2 Torr of He, are summarized in Table II. As a check on the results in He, duplicate measurements were made in Ar carrier for a few cases; the agreement was generally satisfactory. The CF_2Cl_2 and $CFCl_3$ reactions had been studied earlier in a more qualitative fashion.^{9(a)} The agreement is moderately good, but it should be remembered that the absolute uncertainty in measurement of small branching fractions from relative emission intensity data is often higher than suspected.9(b),19

Similar measurements were done for $k_{KrCl^*}^{RCl}$, but CFCl₃ was used as the reference in order to avoid the need to rou-

TABLE II. Rate constant summar	y for $Xe(^{3}P)$	2) at 300 K.
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			$k_{\rm XeCl}$ (10 ⁻¹⁰ cm ³ s ⁻¹)			
Reagent	$(10^{-9} \text{ cm}^3 \text{ s}^{-1})$	$(10^{-10} \mathrm{cm}^3 \mathrm{s}^{-1})$	He	Ar	C/B^{f}	
CF ₂ Cl ₂	3.2	1.9 ± 0.2	0.025	$(0.026 \pm 0.005)^{d}$	0.06	
CF ₂ ClBr	16	4.0 ± 2	~0.015 0.38 [#]	(0.17) ^d	0.54 ^h	
CFCl ₃	260	3.3 ± 0.3	0.56	(∼0.50) ^d	0.15	
$1,2-C_2F_4Cl_2$	0.7	3.5 ± 0.6	0.058	(0.065) ^e	0.30	
$1, 1-C_2F_4C_2$	4.8	3.6 ± 0.6	0.14	(0.15)°	0.31	
1,1,2-C ₂ F ₃ Cl ₃	11	3.7 ± 0.6	0.26	• • •	0.34	
1,1,1-C ₂ F ₃ Cl ₃	280	4.9 ± 0.8	1.91		0.28	
$1,2-C_3F_6Cl_2$	• • •	3.6 ± 0.7	0.25	• • •	0.32	
1,1,1,2-C ₂ H ₂ Cl ₄		••••	~0.02		> 0.02	
CF ₃ CCl=CCl ₂	• • •	• • •	~0.005		0.02	
CF ₃ CH ₂ Br	• • •	• • •	0.34 ^g		0.37 ^h	
Cl ₂	2.0	7.2	7.2		0.22	

 * The rate constant for attachment of thermal electrons from Ref. 19; the value for CF₂ClBr was estimated from

CF₃Br. Recent measurements from Ref. 31 favor somewhat smaller values for CFCl₃ and CF₃CCl₃.

^b The total quenching rate constant taken from Ref. 11 for Cl₂, CF₂Cl₂, and CFCl₃; see the text for the other data.

^cAssigned from relative slopes of plots of I_{XeCl^*} vs [RCl] in He carrier gas (see Fig. 4) with $k_{XeCl}^{Cl} = 7.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which was obtained previously (Ref. 8); $\Gamma_{XeCl^*}^{Cl} = 1.0$. The uncertainty in the k_{XeCl} values is $\pm 20\%$.

^d Independent measurement from plots of I_{XeCl^*} vs [RCl] with Cl₂ as the reference reaction [Ref. 8(b)].

^eIndependent estimate using Cl₂ as the reference reaction, but only for a single concentration (Ref. 11).

^fThe C/B ratio recorded in 2 Torr of He; considerable $C \rightarrow B$ transfer has occurred at this pressure.

⁸ These values are for the formation of XeBr*.

^h The C/B ratio for XeBr* at 2 Torr of He.



FIG. 5. The plot of I_{KrCl^*} vs added [RCl] for the same concentration of $Kr({}^{3}P_2)$ in 3 Torr of He carrier gas. A—Cl₂×300, B—1,1,1-C₂Cl₃F₃×10, C—CCl₃F×10, D—1,2-C₃Cl₂F₆×1, E—1,1,2-C₂Cl₃F₃×1. The numbers denote the factors by which the intensity should be multiplied.

tinely record the KrCl(*B-X*) emission from Kr(${}^{3}P_{2}$) + Cl₂ that falls below 200 nm.¹⁹ All experiments were done in He to avoid possible complications from the presence of a minor concentration of Ar(${}^{3}P_{0,2}$) atoms. The $k \frac{\text{CFCl}_{3}}{\text{KrCl}^{4}}$ value was as-

TABLE III. Rate constant summary for $Kr({}^{3}P_{2})$ at 300 K.

Reagent	Ionization energy (eV)	k_Q (10 ⁻¹⁰ cm ³ s ⁻¹)	Relative slopes ^a	$k_{\rm KrCl^{*}}$ (10 ⁻¹⁰ cm ³ s ⁻¹)	C/B
CFCl,	11.7	4.2(5.1) ^c	1.0	0.05(0.021) ^b	0.54
CF.Cl.	11.8	2.3	• • •	~0.01 ^d	0.32
1.2-C-F.Ch	12.2		• • •	~0.02 ^d	0.48
1.1-C.F.Cl.	~11.8		• • •	~0.02 ^d	0.5
11.1-C-E-CL	11.5		2.31	0.4	0.64
1 1 2 C.F.Cl.	12.0	(4,1) ^c	0.32	0.02	0.74
1.2.0.2.3013			0.45	0.02	0.58
Cl ₂	11.5	7.2	125	6.3	0.42

* Relative slopes from plots of I_{KrCl} , vs [RCl] in 2 Torr He (see Fig. 5) measured at the peak position of the KrCl(*B-X*) spectrum; the k_{KrCl}^{CFCl} value of 0.05×10^{-10} cm³ s⁻¹ was obtained in this work by comparison with

 Cl_2 as the reference reaction. The uncertainty in the reported k_{KrCl^*} values is $\pm 20\%$. ^bAssigned from an independent comparison with the Cl_2 reaction [Ref. 9(c)], but only for a single RCl con-

Assigned from an independent comparison with the C_{12} reaction [real $\gamma(0)$], out only for a single reaction centration.

^c Assigned from observing the variation of the $Kr(5s[3/2]_2^0-5p[5/2]_3)$ transition at 811.3 nm in fluorescence from irradiation from a pen-ray lamp vs [RCl] in 2 Torr He using Cl₂ as a reference (Ref. 15). The fluorescence signal was corrected for optical depth to compensate for self-absorption.

^d An independent estimate using CFCl₃ as the reference reaction, but only for a single concentration in Ar buffer gas at a pressure of 3 Torr.

signed previously using Cl₂ as the reference reaction, ^{9(c)} but it was remeasured in this work. The results from experiments in 2 Torr of He are shown in Fig. 5 and summarized in Table III. In general, the $k_{\rm KrCl}^{\rm RCl}$ values are lower than the $k_{\rm Xecl}^{\rm RCl}$ values, reflecting the less successful competition in reaching the $V({\rm Kr}^+;{\rm RCl}^-)$ ion-pair potential vs the excitation-transfer exit channels. Penning ionization of these molecules by ${\rm Kr}({}^{3}P_{2})$ requires another 1.0–1.5 eV of energy and is not important. The trends in the magnitude of $k_{\rm KrCl}^{\rm RCl}$ and $k_{\rm Xecl}^{\rm Rcl}$ generally correlate with the magnitudes of the thermal electron attachment rate constants of RCl.²⁰ The CF₃CCl₃ molecule is an especially good Cl donor and the branching fraction for XeCl* approaches 0.4, which is comparable to the best polyatomic Cl donors.^{11,19}

The total quenching rate constants for $Xe({}^{3}P_{2})$ were measured by using the quenching rate of $CF_{2}Cl_{2}$ to calibrate the effective flow time. Thus, the total quenching rate constants in Table II are relative to $k_{CF_{2}Cl_{2}}$. All the rate constants for the ethanes are similar and approximately equal to $k_{CFCl_{3}}$. The details associated with these quenching measurements will be reported in Ref. 15.

Diagnostic tests for vibrational enhancement of XeCi* formation

Given the history for incorrect claims of enhancement of bimolecular reactivity by vibrational energy, tests were designed to eliminate alternative explanations of the laser enhanced XeCl^{*} yield before making systematic studies of the vibrational enhancement factors. Some possibilities that were considered are electrical interference from the laser discharge, multiphoton absorption by Xe(${}^{3}P_{2}$), heating of thermal electrons by the laser field, and reactions of Xe(${}^{3}P_{2}$) or Kr(${}^{3}P_{2}$) with the *products* from multiphoton initiated unimolecular reactions. Although electrical interference from the CO₂ laser discharge caused difficulty with signal recording in the original work,⁸ the improvements mentioned in the experimental section largely eliminated the electrical interference. With these improvements, there was no enhancement of signal when the laser was fired in the absence of [RCl]. The possibility that the laser field altered the $Xe({}^{3}P_{2})$ state was eliminated by doing experiments with $Xe({}^{3}P_{2}) + N_{2}$. Even at a laser fluence of 1 J cm⁻², there was no change in the nature of intensity of the $N_2(B^3\Pi_g, v')$ product emission. The possible role of collisions by electron was eliminated by doing experiments in which the laser wavelength was detuned from the absorption bands of CF_2Cl_2 at a fluence of 1 J cm⁻². Over the wavelength range of 1000 ± 200 cm⁻² (see Fig. 2) there was no enhancement of XeCl[‡] yield in either He or Ar carrier. However, tuning the laser wavelength to either the 1100 or 925 cm^{-1} absorption bands gave enhanced XeCl^{*} emission from CF₂Cl₂.

The most difficult question to experimentally eliminate was the possibility of XeCl* formation from a product generated by multiphoton-induced unimolecular reaction. Without doubt, reagents could be selected for which multiphoton-induced decomposition would lead to reaction between the $Xe({}^{3}P_{2})$ or $Kr({}^{3}P_{2})$ atoms and the decomposition products. However, we reject this possibility as the explanation for the enhanced XeCl(B,C) yields with the chlorofluoromethanes and ethanes. We tested for unimolecular reaction by irradiating (R 38 line) a 2 Torr sample of CF₂Cl₂ in a 10 cm cell with $\phi \leq 1$ J cm² with 100 pulses. There was no detectable change in the overall infrared absorption spectrum in the irradiated sample. This conclusion is consistent with prior studies of the multiphoton-induced unimolecular reactions of CF₃Cl and CF₂Cl₂ for which unimolecular reaction was minimal for $\phi \leq 1.5 \text{ J cm}^{-2}$; see references in the earlier report.⁸ Thus, it is impossible for products arising from a single laser pulse to give the observed large enhancement in



FIG. 6. The plots of XeCl^{*} enhancement profiles from $1,1-C_2F_4Cl_2$ following irradiation with $\phi = 1.0$ J cm⁻² at 2 and 5 Torr of He. Each profile is scaled to the same height. The laser pulse, profile number 1, is also shown for reference. The steady-state XeCl^{*} signal is the reference, i.e., the zero level signal is not shown.



FIG. 7. The plots of XeCl^{*} enhancement profiles from $1,2-C_3F_6Cl_2$ following irradiation with $\phi = 1.5$ J cm⁻² in 2 Torr of He and Ar. Each profile is scaled to the same height. The XeCl^{*} steady-state signal level is the reference, i.e., the zero level signal is now shown. The laser pulse, profile number 1, is shown for reference.

XeCl* yield via a secondary reaction. In addition, the decay times for the XeCl* and KrCl* laser enhanced signals (to be presented in the next section) are inconsistent with XeCl* or KrCl* formation from a product of a secondary reaction. If a product from the laser-induced reaction was responsible for the enhancement, the XeCl* decay time should be just the time for the irradiated volume of gas to flow out of the observation zone, and this is not the case. We conclude that the enhanced XeCl* and KrCl* yields arising from the passage of a CO₂ laser pulse through the reaction zone arise from the reactions of vibrationally excited RCl[‡] molecules and *not* from any decomposition products.

Laser enhanced XeCI* and KrCI* formation

The laser enhancement experiments were done with [RCl] $\sim 2 \times 10^{12}$ molecule cm³ and 2 Torr of He or Ar, unless pressure related effects were being studied. The collision frequencies of $CF_2Cl_2^*$ in 2 Torr of He and Ar are $\sim 3.7 \times 10^7$ and $\sim 1.6 \times 10^7$ s⁻¹, respectively, so ~ 35 and ~ 15 collisions of He and Ar occur during a 1 μ s laser pulse. These collisions can either aid or hinder multiphoton energy absorption depending upon the importance of particular quantum states involved in the multiphoton absorption process. Some typical XeCl(B) and KrCl(B) enhancement profiles acquired from the average of 100 laser pulses are shown in Figs. 6-8. The initial rise of the enhanced XeCl* or KrCl* signal from all reagents coincides with the 100 ns spike of the CO_2 laser pulse. The enhanced signal continues to increase until the laser pulse terminates and the energy contained in the tail of the laser pulse is clearly effective in generating vibrationally excited RCl[‡] molecules. In our previous work, there was some concern the about the interpretation of the



FIG. 8. Plots of XeCl* and KrCl* enhancement profiles from CF_2Cl_2 following irradiation with $\phi \gtrsim 0.7 \text{ J cm}^{-2}$ in 2 Torr of He and Ar. Each profile is scaled to the same height. The steady-state XeCl* signal level is the reference, i.e., the zero level signal is not shown. The laser pulse, profile number 1, is included for reference.

XeCl* decay profiles.⁸ But in this work, the expected temporal behavior for the XeCl* and KrCl* enhanced signals following laser excitation was observed for all reagents. Within the experimental uncertainty of the new measurements, the XeCl* and KrCl* decay rates are single exponential; the first-order decay constants depend upon carrier gas pressure and the RCl molecule in question. The delayed maxima in the enhancement profiles for CF₂Cl₂, CFCl₃, and CF₂ClBr, relative to the chlorofluoroethanes, in a consequence of the slower vibrational relaxation rates of the methanes, *vide infra*.

The vibrational enhancement factor F_{ϕ} is defined as the ratio of the maximum laser-enhanced XeCl* or KrCl* signal divided by the steady-state signal for 300 K conditions. These factors are summarized in Table IV for $\phi = 1 \text{ J cm}^{-2}$ and 2 Torr pressure. Experiments were done to record the vibration enhancement factors from CF₂Cl₂ and 1,2- $C_3F_6Cl_2$ by observing both the *B*-X and *C*-A emissions for XeCl* and KrCl* with the monochromator. These experiments were done at 1 Torr of He so that the degree of $C \rightarrow B$ transfer was minimized. In each case, the enhancement factors based upon observing either the B or C states were nearly the same. Therefore, all other enhancement factors were measured by observing the stronger B-X emission. The enhancement factors depend upon the RCl molecule, the laser fluence (see Fig. 9), and less strongly on the pressure and nature of the carrier gas. The enhancement factors for the dichloroethanes 1,1,2-C₂F₃Cl₃, and dichloropropane are quite significant (6–15) and similar to that for CF_2Cl_2 . The $F_{\phi}^{\text{XeCl}*}$ and $F_{\phi}^{\text{KrCl}*}$ values for CFCl₃ are smaller than for CF₂Cl₂, but measurable. The smaller value is expected because Γ_{XeCl^*} is relatively large for CFCl₃, even for 300 K conditions (see Table II), and vibrational energy is not needed to aid the electron transfer product channel; the absorption cross section also is lower than for CF_2Cl_2 (see Table I). Unfortunately, the absorption band for CF₃CCl₃ is outside

TABLE IV. Summary of vibrational enhancement factors.*

·	F_{ϕ}^{Xec}	F ^{KrCl*}	
Molecule	Ar	He	He
$CF_2Cl_2(R_{18})$	20 ± 3	15 ± 2	20 ± 3
$CF_2Cl_2(P_{42})$	10 ± 1	7 ± 1	12 ± 2
$\operatorname{CFCl}_3(R_{38})$	2 ± 0.5	1.5 ± 0.3	2.5 ± 0.3
$1,2-C_2F_4Cl_2(P_{42})$	7 ± 1	6±1	10 ± 3
$1,1-C_2F_4Cl_2(P_{42})$	6 ± 1	6 ± 2	20 ± 5
$1,1,2-C_2F_3Cl_3(P_{14})$	4 ± 1^d	3 ± 1ª	
$1,2-C_{3}F_{8}Cl_{2}(R_{8})$	6 ± 1	4 ± 1	15±6
$CF_2ClBr(R_{36})$	≈7±2	$\approx 6\pm 2$	с
$CF_2ClBr(R_{36})$	3 ± 1 ^b	2.5 ± 0.5 ^b	с
$CF_3CH_2Br(R_{26})$	2.0 ± 0.3	1.3 ± 0.2	c

 ${}^{a}F_{\phi}$ is the ratio of the maximum in the enhancement profile, measured at 1 J cm⁻² and 2 Torr, to the steady-state 300 K signal.

^b The upper entry is the XeCl^{*}; $F_{X^{\text{cBr}}}^{\text{cBr}}$ was measured at 278 nm. The XeCl^{*} measurements were done at 6 Torr in order to minimize the XeBr(C-A) emission, so that XeCl(B-X) could be more easily observed.

^c The $F_{\phi}^{\text{KrBr}*}$ were not studied due to the difficulty of monitoring KrBr(B-X) at 205 nm.

^d The ϕ for 1,1,2-C₂F₃Cl₃ was only 0.7 rather than 1.0 J cm⁻². A linear scaling suggests $F_{\phi} = 5-6$ for the same fluence as the other experiments in the table. The vibrational enhancement factor for CF₃CCl₃ could not be studied because of the low laser fluence for the P_{48} line.

the range of our CO₂ laser and vibrational enhancement experiments could not be done. The $F_{\phi}^{\text{KrCl}*}$ values for the ethanes tend to be somewhat larger than for $F_{\phi}^{\text{XeCl}*}$.

Bromochlorodifluoromethane is an especially interesting case because of the two product channels. Vibrational energy does aid XeBr* formation with a modest enhancement factor of ~ 3 , which is consistent with the larger Γ_{XeBr*}



FIG. 9. Plots of enhancement factors for XeCl* from CF_2Cl_2 (\bigoplus) and 1,2-C₂F₄Cl₂ (\triangle) vs laser fluence from experiments in 2 Torr of Ar.

at 300 K. The more interesting point is that the minor channel, XeCl* formation, is enhanced by vibrational energy more than is XeBr* formation. The enhancement factor for CF_3CH_2Br is small, but significant, at 1 J cm⁻². The enhancement factors are approximately linear with fluence as shown by Fig. 9 for XeCl^{*} formation from CF₂Cl₂ and from $1,2-C_2F_4Cl_2$. A similar fluence dependence was found for KrCl* formation from CF₂Cl₂ and for each of the other reagents that was investigated. The maximum fluence that could be studied was $\sim 1.5 \text{ J} \text{ cm}^{-2}$ because fluorescence from the windows became a problem at higher fluence. Increasing the fluence has two main effects upon the energy absorption by these small molecules: (i) the average number of photons absorbed per molecule is larger for the fraction of molecules participating in multiphoton absorption; and (ii) the fraction of the molecules absorbing energy from the laser field increases for higher fluence. We expect that it is the larger fraction being excited that is mainly responsible for the linear increase of XeCl* (or KrCl*) enhancement with φ.

Survey experiments were done with different laser wavelengths; enhancement occurred only when the laser wavelength matched an absorption band. Larger $F_{d}^{\text{XeCI}*}$ were observed when the laser was tuned to the red of the maximum of the absorption band, whereas tuning to the blue side always gave diminished $F_{\phi}^{\text{XeCl}*}$. Such a dependence on laser wavelength is expected for a process that depends upon multiphoton absorption, because of the anharmonic shift for higher levels of the pump mode. The dependence of $F_{\star}^{\text{XeCl}*}$ upon excitation of the 1100 and 925 cm^{-1} bands of CF_2Cl_2 was specifically investigated. The time profiles of the enhanced signals were both the same, but $F_{\phi}^{\text{XeCl}*}$ and $F_{\phi}^{\text{KrCl}*}$ were about twofold larger [see Table IV] for the 1100 cm^{-1} band (which is the C-F stretch mode). This result is consistent with the larger effective multiphoton absorption cross section at the 1089 cm^{-1} wavelength.^{8,21}

Collisions during the laser pulse can relieve rotational bottlenecking, leading to a higher fraction of RCl molecules that absorb laser energy, but collisions with RCl[‡] molecules also can deactivate high vibrational levels during the terminal part of the laser pulse. Thus, increasing He and Ar pressure could either decrease or increase the vibrational enhancement factors depending upon which relaxation process was more important. As already noted, the rise times for XeCl* or KrCl* formation were independent of pressure. Increasing the He or Ar pressure shortened the decay times, but changes in the enhancement factors with pressure were very modest. In general, there was a slight increase in $F_{\phi}^{\text{XeCl}*}$ or $F_{\phi}^{\text{KrCl}*}$ from 1–4 Torr followed by a reduction in the 4–10 Torr regime. The $F_{\phi}^{\text{XeCl}*}$ were slightly larger in Ar than in He. The major effect of pressure upon the laser-enhanced signals certainly is associated with vibrational deactivation of RCl[‡], as exemplified by the pressure dependence of the decay rates, and not upon the multiphoton excitation processes.

Collisional relaxation rates of RCI[‡] molecules

The laser-enhanced XeCl* and KrCl* signals decayed exponentially. The pressure dependence of these decay con-



FIG. 10. Plots of XeCl* decay constants from A—CF₂Cl₂ in Ar, B— CF₂Cl₂ in He, C—1,2-C₂Cl₂F₄ in He, and D—1,2-C₂Cl₂F₄ in Ar.

stants is plotted for several examples in Fig. 10. The decay constants were linear with either He or Ar pressure; the decay constants at 2 Torr and the two-body relaxation constants are summarized in Table V. The same decay constants were found for monitoring either KrCl* and XeCl*, showing that relaxation involves collisions of the RCl[‡] molecules with He or Ar. The relaxation rates of CF₂Cl₂ and CFCl₃ are similar, and the rate constants in He are fourfold larger than in Ar. The relaxation rate constants for the chlorofluoroethanes and propane tend to be similar, but larger than for the chlorofluoromethanes. For the larger molecules, the rate constants in He and Ar are the same to within the experimental uncertainty. The plots in Fig. 10 imply a small nonzero intercept for the zero pressure decay time. This is expected because at low pressure the residence time for the irradiated gas volume becomes comparable to the collisional relaxation time. We had some concern about the interpretation of the position of the maximum in the profiles of the chlorofluoromethanes vs the chlorofluoroethanes. Therefore, a computer code was developed to simulate the rate equations corresponding to Eqs. (1), (2), and (3) together with the collisional relaxation of RCl[‡]. The rate of formation of [RCl[‡]] was represented by a simple exponential function with a 2 μ s decay constant. The simulated and experimental results, which are compared in Fig. 11, are in close agreement. The delayed maximum of the enhanced signal from the chlorofluoromethane is a consequence of the slower collisional vibrational relaxation rate and not a property of the multiphoton laser-excitation mechanism. Time-dependent Raman scattering studies have shown that the internal relaxation times for CF₂Cl₂ is of the order of 100-200 ns following CO₂ laser excitation.²² This is shorter than the rise time for the XeCl* enhanced signal from CF2Cl2, which follows the CO_2 laser pulse. For the μ s time scale of our experiments, collisions and internal relaxation ensure that the vibrational energy absorbed from the laser pulse is statistically distributed within a given RCl[‡] molecule.

We will discuss two interpretations of the rate constants given in Table V. The possibility that the observed relaxation

		Ar		Не	
Molecule	(10 ⁴ s ⁻¹) ^b	k _R ^c	(10 ⁴ s ⁻¹) ^b	k _R °	
$CF_2Cl_2(R_{38})$	2.8 ± 0.3	$3.1 \pm 0.3 \times 10^{-13}$	11.0 ± 1.5	$13 \pm 2 \times 10^{-13}$	
$CF_2Cl_2(P_{42})$	2.7 ± 0.3	$3.1 \pm 0.3 \times 10^{-13}$	11.0 ± 1.5	$13 \pm 2 \times 10^{-13}$	
$\operatorname{CFCl}_3(R_{38})$	2.8 ± 0.3	$3.2 \pm 0.3 \times 10^{-13}$	10 ± 2	$14 \pm 2 \times 10^{-13}$	
$1,2-C_{2}F_{4}Cl_{2}(P_{42})$	37 ± 5	$46 \pm 8 \times 10^{-13}$	30 ± 5	$46 \pm 7 \times 10^{-13}$	
$1, 1-C_2F_2Cl_2(P_{42})$	35 ± 5	$53 \pm 8 \times 10^{-13}$	30 ± 5	$60 \pm 8 \times 10^{-13}$	
$1,2-C_3F_6Cl_2(R_8)$	40 ± 10	$70 \pm 8 \times 10^{-13}$	50 ± 10	$70 \pm 9 \times 10^{-13}$	

TABLE V. Relaxation constants at 2 Torr and two-body rate constants.

^a Measured for fluences near 1 J cm⁻².

^bDecay constants at 2 Torr pressure.

^c Two-body relaxation rate constant (cm^3 molecule⁻¹ s⁻¹) from plots of the decay constants vs pressure.

is just V-T transfer from the lowest vibrational mode is examined first. The second, and favored, interpretation is that the exponential decay rate is associated with overall relaxation of the mean vibrational energy $\langle \Delta E_{\mu} \rangle$ of the RCl[‡] molecules. The relaxation rate constants that we obtained for CF_2Cl_2 can be compared to results in the literature.²³ Using the time-resolved thermal lensing technique following excitation of $v_6(992 \text{ cm}^{-1})$, rate constants of $26 \pm 7 \times 10^{-13}$ and $2.7 \pm 0.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were reported^{23(a)} for the V-T relaxation of CF₂Cl₂ by He and Ar, respectively. These rate constants were associated with the V-T relaxation rates from the lowest vibrational mode, which is $v_4(261 \text{ cm}^{-1})$ for CF₂Cl₂. This rate constant for Ar, as well as one for more extreme laser pumping,^{23(b)} is in excellent agreement with our value, but our result for He is a factor of 2 smaller than theirs. The lowest vibrational frequency for the chlorofluoroethane molecules is the torsional mode associated with internal rotation ($<90 \text{ cm}^{-1}$); larger relaxation rate constants with weaker dependence on mass of the collisional partner, would be expected for V-T relaxation via such a low frequency,^{23,24} relative to the chlorofluoromethanes. To our knowledge, measurements of the V-Trelaxation rates for the chlorofluoroethane molecules in He and Ar have not been reported. Although the comparisons



FIG. 11. Comparison of the experimental enhancement profiles for XeCl^{*} from CF_2Cl_2 and $1,2-C_2F_4Cl_2$ in 1 Torr of Ar vs their simulated profiles using experimental rate constants (see the text). Note that the position of the delayed maximum in the profile for CF_2Cl_2 is reproduced by the simulation.

just made seem to argue for V-T relaxation from the lowest frequency mode, such an interpretation is not consistent with our understanding of infrared multiphoton excitation. Furthermore, more than a few quanta of excitation in the lowest frequency vibration is probably needed to enhance reaction (3a). An alternative point of view is that the XeCl* decay is monitoring the relaxation of the average energy $\langle \Delta E_n \rangle$ of the multiphoton pumped molecules.²⁵ The overall SF₆,^{25(a)} vibrational relaxation of CF₃I,^{25(b)} CF₂H-CFH₂,^{25(c)} and some perfluorinated molecules^{25(d)} excited to high vibrational levels has been monitored by several physical methods. In each case, the rate constants for relaxation in Ar are of the same magnitude as those given in Table V. We conclude that the XeCl* decay rate is reflecting the exponential relaxation of the average vibrational energy of the RCl[‡] molecules. After adjustment for the different collision rates of He and Ar, the collisional efficiency of Ar with the ethanes would be higher than for He, as expected for highly vibrationally excited molecules.²⁵ However, the efficiency for He is still larger than for Ar with the methanes. even after adjustment for the collision rates. This may reflect the sparse density of states in the relevant energy regime for the chlorofluoromethanes. Based upon energy absorption measurements⁸ for these and similar molecules, we expect $\langle n \rangle$ to be in the range of 10–20 photons molecule⁻¹ for $\phi \simeq 1 \, \mathrm{J} \, \mathrm{cm}^{-2}$.

DISCUSSION AND CONCLUSIONS

The trend in the room temperature Γ_{XeCl^*} and Γ_{KrCl^*} values for the chlorofluorethanes provides another example²⁶ of the correlation between the magnitudes of the dissociative, thermal electron attachment rate constants β , and the branching fractions for reactive quenching, i.e., XeX* and KrX* formation. Thermal electron attachment is best understood for the chlorofluoromethane series. The activation energy for thermal electron attachment have been assigned as ~0(CCl₄),^{19(a)} ~2 kJ/mol (CFCl₃),^{19(a)} 12 kJ/ mol (CF₂Cl₂),^{19(a)} and ~75 kJ/mol (CF₃Cl).²⁷⁻³⁰ The most recent work suggests that there is no true activation energy for CFCl₃.³¹ The small difference in β for CCl₄ and CFCl₃, a factor of 2 at 300 K, still seems to relate to the Xe(³P₂) and Kr(³P₂) reactions because $\Gamma_{XeCl}^{CCl_4}$ (0.27) is larger than $\Gamma_{XeCl^{*}}^{CFCl_{3}}(0.17)$. The electron enters a σ^{*} antibonding type orbital, and the main changes in CCl_4^- and $CFCl_3^-$, relative to the neutral molecules, are a partial flattening of the pyramidal CCl₃ group and lengthening of those C-Cl bonds.³² The *ab initio* calculations^{32,33} and the model³¹ used for calculation of attachment cross sections suggest intersection of the neutral and radical anion potentials in the thermally accessible region of the neutral potential; however, there has been a question³² about whether the optimum geometry was explored for the CFCl₃⁻ calculation.³³ The β for a third molecule, CF₃CCl₃ is in the 250×10^{-9} cm³ s⁻¹ range and the branching fraction for XeCl* formation also is large, $\sim 0.2.^{34}$ The kinetic energy released to Cl⁻ is nearly statistical for attachment to CCl₄ or CFCl₃, but the kinetic energy³⁴ is 0.34 eV for CF_3CCl_3 . However, this exit channel effect does not seem to influence Γ_{XeCl^*} .

The Γ_{KrCl}^{RCl} for both the chlorofluoroethanes and chlorofluoromethanes is lower than for Γ_{XeCl}^{RCl} because excitation transfer is more dominant for quenching of $Kr({}^{3}P_{2})$. Excitation transfer probably arises from the coupling of the entrance channel to Rydberg states before the collision pair reaches the ion-pair potential at short range. Since the density of RCl** Rydberg states at 10.5 eV is larger than at 8.3 eV, there is a greater probability for excitation transfer during the incoming trajectory for $Kr({}^{3}P_{2})$ than for $Xe({}^{3}P_{2})$.

Our novel finding is the demonstration that vibrational energy in chlorofluoromethanes and chlorofluoroethanes can greatly change the chemical product distributions from quenching of $Kr({}^{3}P_{2})$ and $Xe({}^{3}P_{2})$ atoms. The vibrational energy enhancement of XeCl* or KrCl* formation is largest for those molecules with small Γ_{XeCl}^{Rel} and Γ_{KrCl}^{RCl} at 300 K. The $Xe({}^{3}P_{2})$ reaction with HCl is another reaction showing vibrational energy enhancement.³⁵ Since the total quenching rate constants for 300 K conditions are quite large, the vibrational energy enhancement is associated with larger branching factors for XeCl* or KrCl* formation in competition with the excitation-transfer channel and not in appreciably larger k_0 . For these small molecules, rotational bottlenecking during multiphoton absorption leads to fractionation of the thermal ensemble of molecules^{8,12} and the enhancement factors of Table IV are lower limits to the true enhancement factors, i.e., if all RCl molecules were vibrationally excited, the F_{ϕ} values would be even larger. Previous estimates⁸ for the fraction of CF₂Cl₂, CFHCl₂, and CF₃Cl molecules absorbing laser energy suggested that the true branching fractions for XeCl^{*} formation for these molecules might be ~ 0.5 . The degree of fractionation should be smaller for the ethanes than for the methanes, so the true branching fractions for XeCl* formation from vibrationally excited ethanes will not be as large as for the methanes. The XeCl(B,C)and KrCl(B,C) vibrational energy distributions from reaction with the RCl[‡] molecules probably extend to higher vibrational energy than for 300 K reactions, but that aspect of the dynamics for RCl[‡] molecules has not yet been investigated.

The dynamics required to explain the vibrational energy enhancement of XeCl* or KrCl* formation is probably related to the same factors that are responsible for the increase in dissociative electron attachment rates by vibrational excitation.^{20,27-29} The increase in the total energy of the $Xe^* + RCl$ collision may be of some importance too, because the electron affinity values for the chlorofluoromethanes and chlorofluoroethanes are modest and the diabatic crossing of $V(Xe^*,RCl)$ and $V(Xe^+,RCl^-)$ is at short range with a threshold energy. To our knowledge the dependence of XeCl* formation on translational energy has not been studied by molecular beam methods for these molecules. By analogy to other cases,³⁶ the increased total energy may aid XeCl* formation. Certainly higher electron energy results in larger electron attachment cross sections for molecules with threshold energies. However, we believe that the XeCl* and KrCl* enhancement has its origin mainly in vibrational energy, rather than just the higher total energy of the collision.

In the comments to follow, an intrinsic assumption will be that XeCl* or KrCl* formation is efficient after the Xe*-RCl[‡] or Kr^{*}-RCl[‡] collision pair reaches the crossing region for the ion-pair potential. The possibility for transfer from $V(Xe^+, RCl^-)$ back to $V(Xe, RCl^*)$ will not be emphasized.36(e) Another clue about the dynamical origin of the vibrational energy enhancement can be gained from the comparison between the reactivity of Xe(6s) and Xe(6p) atoms with CF_2Cl_2 and CF_3Cl (and HCl), the Xe(6p) atoms have much larger $\Gamma_{XeCl^*}^{RCl}$ values.^{8,37} This is easily explained from the location of the crosssing between the $V(Xe^+, RCl^-)$ and $V(Xe^*,RCl)$ diabatic potentials, which moves to longer range for V[Xe(6p), RCl]. Thus, the incoming collision pair can transfer to the ion-pair potential before the Xe(6p)-RCl collision samples the region where coupling to the RCl* Rydberg background states becomes strong. By similar reasoning, vibrational energy must provide a mechanism for coupling the V[Xe(6s),RCl] and $V(Xe^+,RCl^-)$ potentials at a larger Xe(6s)-RCl[‡] distance than for a collision without vibrational energy. Given the structural changes in the radical anion vs the RCl molecule, the vibrational motions responsible for the coupling presumably are a combination of C-Cl bending and C-Cl stretch modes. Since the vibrational periods are somewhat shorter than the mean collision time (~ 0.6 ps), the internal coordinates of RCl[‡] will be sampled during a thermal collision. In a simple point of view, the vibrational energy acts to increase the vertical electron affinity, which promotes the transfer to $V(Xe^+,RCl^-)$ at long range. Inspection of the CFCl₂-Cl and CFCl₂-Cl⁻ potentials³¹⁻³³ shows that stretching of F(C-Cl) does increase the E.A. Thus, this point of view has some merit. Another aspect could be that vibrational excitation inhibits coupling to the background RCl* Rydberg potentials, which would allow the incoming trajectory to reach $V(Xe^+,RX^-)$ at short range. However, we do not see a reason why vibrational energy would inhibit such a coupling for all members of the class of molecules investigated in this work.

In summary, a class of polyatomic RCl molecules has been discovered for which vibrational energy alters the product distribution from collisional quenching of $Xe({}^{3}P_{2})$ and $Kr({}^{3}P_{2})$ atoms. Enhancement of reactive quenching, i.e., XeCl* or KrCl* formation, by vibrational energy in competition with excitation transfer should occur with other reagents for which vibrational energy aids dissociative thermal electron attachment. As the role of vibrational energy upon electron attachment rates by polyatomic molecules is better understood, insight will be gained about the dynamics for this category of reaction. In order to reach more quantitative interpretation about the dependence of the branching fraction on vibrations energy, independent work is needed to characterize the fraction of molecules absorbing energy from the field and their average level of energy for a given laser fluence. The decay of the XeCl* vibrationally enhanced signal was associated with the exponential relaxation of the average vibrational energy of the RCl[‡] molecules from collisions with He or Ar.

Note added in proof: Professor J. Simons and co-workers (University of Nottingham) soon will publish data which demonstrate that $k_{XeCI^*}^{CF_2CI_2}$ also is sensitive to the translational energy. Thus, the XeCl* exit channel from Xe(6s) + CF_2Cl_2 depends strongly upon all of the initial energy states of the reactants.

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