



Statetostate relaxation processes for XeCI(B, C)

T. D. Dreiling and D. W. Setser

Citation: The Journal of Chemical Physics **75**, 4360 (1981); doi: 10.1063/1.442599 View online: http://dx.doi.org/10.1063/1.442599 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/75/9?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

StatetoState Kinetic Theory Approach for Transport and Relaxation Processes in Viscous Reacting Gas Flows AIP Conf. Proc. **1333**, 1371 (2011); 10.1063/1.3562834

State-to-state rate coefficients for rotational relaxation of CO in Ar J. Chem. Phys. **110**, 8513 (1999); 10.1063/1.478759

Statetostate relaxation of highly vibrationally excited acetylene by argon J. Chem. Phys. **101**, 9642 (1994); 10.1063/1.467929

Photoassociative laserinduced fluorescence of XeCl* and kinetics of XeCl(B) and XeCl(C) in Xe J. Chem. Phys. **80**, 6006 (1984); 10.1063/1.446682

Absorption processes in the XeCl laser Appl. Phys. Lett. **34**, 315 (1979); 10.1063/1.90788



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.216.129.208 On: Fri, 05 Dec 2014 04:35:36

State-to-state relaxation processes for XeCI(B,C)

T. D. Dreiling and D. W. Setser

Chemistry Department, Kansas State University, Manhattan, Kansas 66506 (Received 27 March 1981; accepted 9 July 1981)

The XeCl (B-X) and (C-A) emission spectra obtained from reaction of Xe $({}^{3}P_{2} \text{ or } {}^{3}P_{1})$ with Cl₂, CCl₄, and COCl₂ in the presence of He, Ne, Ar, Kr, and N₂ bath gases were used to study the vibrational relaxation and transfer between the *B* and *C* states of XeCl. By using the different Cl donors, different ranges of vibrational energy were emphasized. The bound-free emission spectra were simulated for various pressures of bath gas to obtain vibrational distributions. Numerical modeling of the XeCl(*B*) and XeCl(*C*) vibrational populations and the *B/C* intensity ratio as a function of pressure gave rate constants for vibrational relaxation and transfer, as well as the model for the state-to-state processes. For Ar as the bath gas, vibrational relaxation can be characterized by an exponential gap model $P_{ij} \propto e^{-0.14E/kT}$, with rate constants of (1-6), (6-12), and (20-30) $\times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹ for the *v* ranges of 0-30, 30-70, and 70-130, respectively. The rate constants for electronic state transfer are (3-11), (11-15), and (15-15) $\times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹ for the same *v* ranges. The vibrational energy loss upon electronic state transfer was best described by a Poisson-type function displaced to lower energy from the initial energy. These basic models also describe the relaxation in the other gases with He and Ne being less efficient and Kr and N₂ more efficient than Ar. The magnitudes of the rate constants and the models are discussed.

I. INTRODUCTION

Because of the importance of rare gas halide excimer lasers, considerable research has been directed toward characterizing and understanding the basic kinetic processes of formation, quenching, electronic state transfer, and vibrational relaxation of the B(1/2) and C(3/2)states of the rare gas halide molecules.¹ The importance of the *C* state has only recently been realized. In fact, the *C*-*A* transition of XeF has been made to lase.² Clearly the *C* state must be included in any realistic model of the laser medium, and understanding the B-Cstate coupling and the associated vibrational relaxation may be of importance in optimizing the design and performance of the rare gas halide lasers.

Previous reports from this and other laboratories have provided information concerning the reactions of the first excited states $\operatorname{Rg}({}^{3}P_{2,1})$ of the rare gas atom with halogen donating molecules to form the $\operatorname{RgX}(B, C)$ molecules. Quenching rate constants and branching fractions have been reported for $\operatorname{Ar}({}^{3}P_{2})$, $\operatorname{Kr}({}^{3}P_{2})$, and $\operatorname{Xe}({}^{3}P_{2})$ with a variety of halogen donors. ${}^{3-4}$ In addition, the bound-free emission spectra from the $\operatorname{RgX}(B-X)$ and $\operatorname{RgX}(C-A)$ transitions have been interpreted to provide information concerning the vibrational energy disposal and dynamical features of these reactions. 5,6 Although most of the work has been concerned with the metastable ${}^{3}P_{2}$ state, results for the ${}^{3}P_{1}$ state appear quite similar. 7

In this paper, we present results concerning the vibrational relaxation and electronic state transfer for the XeCl(B, C) states in various bath gases. We chose XeCl because of the ease of obtaining experimental data and because assignment of vibrational distributions from the bound-free spectra is more straightforward. The general findings from the XeCl results should be extendable to other RgX systems. We discuss in detail the results for XeCl* in argon and subsequently contrast the relaxation processes in Ar with those in He, Ne, Kr, Xe, and N₂. The final results are in the form of stateto-state rate constants for C-B transfer and for vibrational relaxation as a function of vibrational level. In addition to applications to rare gas halide lasers, the results are of general interest for relaxation of high vibrational levels of ionic diatomic molecules in rare gases.

Reactive quenching of $Xe({}^{3}P_{2,1})$ with halogen donors gives XeCl(B, C) with various vibrational distributions. and using different donors permits a range of the vibrational levels to be emphasized. For instance, the donors Cl₂, CCl₄, and COCl₂ give vibrational distributions peaking at v = 100, 50, and 0, respectively.^{5(b)} Computer simulation of the B-X and C-A emission spectra permits assignment of the vibrational distribution. Initial distributions are obtained from low pressure (≤ 0.2 Torr) spectra where collisions with the bath gas are not important. At higher pressures the appearance of the B-Xand C-A emissions and their relative intensities change as a consequence of vibrational relaxation and transfer between the two electronic states by bath gas collisions. By modeling the population distributions and the B/C intensity ratios as a function of bath gas pressure, rate constants for relaxation and transfer can be deduced, as well as a state-to-state view of these processes. The state-to-state kinetics are emphasized in this paper; however, the results are of practical relevance because the rare gas halide formation processes in lasers, whether they be reactive quenching of excited rare gas atoms or ion-ion combination, initially yield high vibrational levels of $\operatorname{RgX}(B, C)$.

The organization of the paper is as follows. In Sec. II the experimental results for the reactions of $Xe({}^{3}P_{2,1})$ with Cl_{2} , CCl_{4} , and $COCl_{2}$ in various bath gases are summarized. Also the XeCl(B, C) vibrational distributions obtained from simulation of spectra are presented. The XeCl(B-X) and XeCl(C-A) simulation is nearly the same as used previously^{5(b)} and this is only briefly mentioned. Section III gives the details of the modeling procedures used to reproduce the variation of the populations with pressure. The detailed results for Ar are

130.216.129.208 On: Fri, 05 Dec 2014 04:35:36



FIG. 1. Comparison of experimental (---) and simulated (---) spectra of the B-X and C-A emission of XeC1 resulting from the reaction of Xe*+Cl₂ in Ar. In each case the B-X spectra have been attenuated so that the most intense peak of the C-A and B-X emission have the same height.

given in Sec. IV and a summary of the other gases is given in Sec. V. A discussion is given in Sec. VI.

II. EXPERIMENTAL RESULTS AND SPECTRAL SIMULATIONS

The experimental details for study of the $Xe({}^{3}P_{2})$ and $Xe({}^{3}P_{1})$ atom reaction with chlorine donors have been given elsewhere^{3, 7} and can be briefly summarized here. The metastable atom reactions are studied with a flowing afterglow apparatus. A small amount of Xe is entrained in an Ar carrier gas flow which is passed through a low power hollow cathode discharge. $Xe({}^{3}P_{2})$ is formed from direct excitation in the discharge and from excitation transfer from $Ar({}^{3}P_{2}) + Xe$. Only the relatively long lived $Xe({}^{3}P_{2})$ survives the transit time to the reaction zone several centimeters downstream of the discharge. The chlorine donor is added coaxially to the Ar/Xe flow in the reaction zone and the resulting XeCl* emission is observed with a monochromator and detection system interfaced to a minicomputer. The computer controls data acquisition and stores the spectra on magnetic tape for subsequent analysis.⁸ The spectra can be corrected for the spectral response of the detection system, integrated to obtain (B-X) and (C-A) emission intensities, and replotted for direct comparison with simulated spectra. The pressure at which the spectra are observed can be changed by varying the Ar flow and/or throttling the pumping speed. The flowing afterglow method is somewhat limited in that only inexpensive gases (Ar) can be routinely used as the carrier gas and the pressure range is restricted from 0.2 to ~50 Torr.

For the resonance state atom reactions a mixture of

Xe, chlorine donor, and bath gas, under either static or flowing conditions, is irradiated in a reaction cell with a microwave powered Xe resonance lamp interfaced to the cell with a MgF₂ window. Radiation trapping in the cell lengthens the effective lifetime of $Xe({}^{3}P_{1})$ to a time scale permitting reaction to occur. The XeCl* emission is observed at right angles to the light from the resonance lamp with the same detection system as above. Relative to the flowing afterglow, this method has the advantage of a much larger pressure range, 0.1 Torr to 5 atm, as well as permitting different bath gases to be used. One disadvantage is scattered light from the discharge, mainly Xe* lines, which overlap the long wavelength part of the XeCl(C-A) spectrum. The intensity of the atomic lines must be carefully subtracted out to obtain accurate B/C intensity ratios. In all of the work here the small (the calculated B-A/B-X branching ratio is 0.06) contribution of the B-A transition to the C-A spectrum has been ignored.

Sample XeCl spectra obtained with the above methods are shown in Figs. 1-3 for various donors and pressures of argon. Although close examination does show slight differences resulting from the 978 cm⁻¹ higher energy for the resonance state, the spectra from the $Xe({}^{3}P_{1})$ and $Xe({}^{3}P_{2})$ reactions are virtually identical and in the remainder of this paper no distinction will be made between them. Plots of the intensity ratio I_{B}/I_{C} versus pressure are shown in Figs. 4(a) and 4(b) for the reactions of Xe^{*} + Cl₂, CCl₄, and COCl₂ in argon and for Xe^{*} + Cl₂ in various bath gases.

The numerical simulation of the experimental boundfree spectra has been presented elsewhere.⁵ Three



FIG. 2. Same as Fig. 1 but from Xe*+CCl₄. In the 240-260 nm region, the simulated B-X spectra are above the experimental spectra because a flat potential was used for the XeCl(X). The use of a more realistic potential would reduce the intensity by shifting the transition occurring at the inner turning point of the upper state to longer wavelengths.



FIG. 3. Simulated (---) and experimental (---) spectra from Xe*+COCl₂. The lack of oscillatory structure, even at low pressure, prevents a reliable vibrational distribution from being assigned.



FIG. 4. Comparison of the I_B/I_C intensity ratios as a function of pressure for (a) the Cl_2 , CCl_4 , and $COCl_2$ donors in argon and (b) for $Xe^* + Cl_2$ in the various bath gases. The dashed line in b serves only as an aid in identifying the argon points.

basic variables enter into the simulations: relative shapes of the two potentials, variation of the transition moment with internuclear distance, and the vibrational distributions. The variation of the transition moment is especially important in fitting the bound-free emission. In this work we used the procedure developed previously for fitting the XeCl(B-X) emission, which employed Tellinghusin's B state potential in a Rittner form with a flat potential for the X state.^{5(b)} The effects of the transition moment were included by introducing a monotonic function to multiply the spectrum obtained using a constant transition moment. These results were successful in simulating the XeCl(B-X) emission from a variety of donors. The B-X transition is easy to simulate because the spectra are not very sensitive to the shape of the lower potential; such is not the case for the C-A transition, where the repulsive wall for the lower state A-potential is very important. Initially we used the potentials previously employed to simulate the C-Atransition. However, when modeling the XeCl(B) distribution as a function of pressure, a second maximum developed in the distribution from C - B collisional transfer. This second peak, which is not experimentally observed, was a consequence of the initial C distribution having its maximum at lower E_{y} than for XeCl(B). This is evident in Figs. 4 and 7 of Ref. 5(b) where E_{mp} (XeCl, B) is 6 kcal mole⁻¹ larger than E_{mp} (XeCl, C) from the Xe* + Cl₂ reaction. To rectify the problem it was necessarv to make the A state slightly more repulsive so that the vibrational distribution from the C-A emission was moved to higher E_{v} . The initial XeCl(C) distributions used here from Cl₂, CCl₄, and COCl₂ were indistinguishable from the XeCl(B) distributions.

The expressions for the potentials used here to simulate the C-A emission are

$$V(R)^{C,3/2} = \frac{\omega_e^{C,3/2}}{\omega_e^{B,1/2}} V^T(R')_{B,1/2} \,\mathrm{cm}^{-1} , \qquad (1a)$$

$$V(R)^{A,3/2} = 1.77 \times 10^7 \exp(-2.827 R') \text{ cm}^{-1}$$
, (1b)

where $V^{T}(R')_{B,1/2}$ is given by Eq. (4a) of Ref. 5(b), $R' = R_{e}^{B,1/2} + 0.9814(R - R_{e}^{C,3/2}) - 0.0365(R - R_{e}^{C,3/2})^{2}$, $\omega_{e}^{B,1/2} = 195.2 \text{ cm}^{-1}$, $\omega_{e}^{C,3/2} = 188 \text{ cm}^{-1}$, $R_{e}^{B,1/2} = 2.937 \text{ Å}$, and $R_{e}^{C,3/2} = 3.14 \text{ Å}$. It should be noted that the expressions for the A potential and the transition moment function of Ref. 5(b) [Eqs. (14) and (15)] are slightly in error.⁹ Since no empirical potential for the C state was available, Eq. (1a) was used to cast the *ab initio*^{10(ω)} C potential into a form similar to the empirical (Tellinghuisen's) B state potential. However, because of the expression for R', Eq. (1a) is valid only for R less than ~10 Å and should be used with some caution. In addition, the use of an empirical B and ab initio C potential leads to some discrepancies when comparing the R_s 's and ω_e 's of the two states with theoretical predictions. While theoretical calculations^{10(a)} predict a larger R_e and smaller ω_e for XeCl(B), the opposite is the case for the potentials used here. The situation for the R_e 's is not serious for the work described here since both the C and A potentials can be shifted to shorter internuclear distance without affecting the simulations, i.e., only the relative position of potentials is important. The ω_e discrepancy is more serious since it (along with $\omega_e x_e$) describes the energy levels of the two states. Unfortunately, no empirical potential exists for the C state and it was necessary to resort to the ab initio curve.

The basic procedure for simulating the experimental spectra was to first calculate spectra for individual vibrational levels of the upper state. These individual spectra were then summed over an assumed vibrational distribution to obtain a total spectrum. Different vibrational distributions were tried until a satisfactory fit was found for the experimental spectra obtained at different pressures. Some simulated spectra are compared to the experimental ones in Figs. 1-3 and the corresponding steady-state vibrational distributions are shown in Figs. 5-7.

Two important points affecting the modeling are the reliability of the distributions, i.e., how accurate are the simulations, and the variation of the XeCl* lifetime with v level. The first point is addressed in Fig. 8, which shows $XeCl^*(B-X)$ emission spectra in Ar from



FIG. 5. Steady-state XeCl(B, C) vibrational distribution obtained from simulation of Xe^{*}+Cl₂ spectra at various Ar pressures. Because of different ω_e and $\omega_e x_e$ values, the v_{\max} levels for the two states are different, even if the vibrational energy is the same (see Table I).

Xe* + Cl₂ at 1.3 Torr and from Xe* + CCl₄ at 11.9 Torr along with two simulated spectra that were judged to be satisfactory fits. The corresponding vibrational distributions differ by $\sim 10\%$ on the average. Hence any relaxation model that matches a distribution to within $\sim 10\%$ of the distribution assigned by simulation must be considered satisfactory. This 10% uncertainty reflects only the ability to successfully simulate the observed spectra using several assumed distributions, all of which differ by less than 10% on the average. A discussion of errors in the derived population distributions associated with assumptions concerning the potentials involved and the dipole moment functions is presented in Ref. 5(b) and briefly in the Discussion section. The uncertainty in the distributions increases with increasing pressure (reduction in vibrational energy) because of the loss of the oscillations from the spectra. This is evidenced by the spectrum from CCl₄ for which the distributions are less unique than for the low pressure Cl₂ spectra. Above ~15 Torr of Ar the oscillations have disappeared and the best that can be done is to assign high temperature Boltzmann distributions. The above discussion was based on the B-X spectrum. For the

C-A spectra, the potential curves are less accurate and the B-A and C-A emissions overlap; therefore the distributions from the spectral simulations are less reliable than those from the B-X simulations. Hence, in modeling, emphasis was placed first on fitting the $I_B/$ I_C ratio vs pressure, then the B state vibrational distribution, and finally the C state vibrational distribution.

The second point was the variation of the XeCl(B, C)lifetimes with v level. Unfortunately, measurements of the XeCl(B, C) lifetimes have not been reported. However, the theoretical values given by Dunning and $Hay^{10(a)}$ for XeCl(B, v=0), 11 nsec and XeCl(C, v=0), 120 nsec, can be combined with the dependence of the transition moment on internuclear distance to obtain calculated lifetimes. The Einstein coefficients decrease by ~ 3 from v = 0 to 100; therefore the lifetimes increase by ~3. This trend of increasing lifetime vs v level has been observed for a small range of v for KrCl.¹¹ Dunning and Hay have calculated lifetimes for ArF, KrF, and all the xenon halides.¹⁰ Experimental lifetimes have been reported for $KrF(B)^{12(a)}$ and $XeF(B, C)^{12(b)}$; the results generally agree with the calculated values to within ~30%. The XeCl calculated lifetimes and energy levels



FIG. 6. Steady-state XeCl (B, C) vibrational distribution obtained from simulation of the XeCl*+CCl₄ spectra at various pressures of Ar.

J. Chem. Phys., Vol. 75, No. 9, 1 November 1981

130.216.129.208 On: Fri. 05 Dec 2014 04:35:36



FIG. 7. Steady-state XeCl(B, C) vibrational distributions from Xe^*+COCl_2 at 0.1-0.2 and 3-6 Torr. Only the shape of the distributions have significance; note the similarity to Boltzmann distributions.

used in the modeling calculations are summarized in Table I.

Even without the modeling results, some general conclusions can be drawn from the data. 7,13 Although the statements below refer to argon bath gas, the same trends are observed in other bath gases; however, the characteristic pressure regions are different. At zero pressure, the initial I_B/I_C is 1.3-1.5 for all three donors, Cl₂, CCl₄, and COCl₂. In the low pressure $(\leq 5 \text{ Torr})$ regime, B state vibrational relaxation, C state vibrational relaxation, and a rapidly increasing I_B/I_C is observed. Since at these pressures the lifetime of the B state is less than the time between collisions with bath gas, the apparent B state relaxation is due to collisional transfer from the C state. This is also the cause of the increasing I_B/I_C ratio. A simple steadystate analysis for XeCl(B) and XeCl(C) similar to those used previously 4(a), 7 can be used to obtain approximate rate constants for C to B transfer k_{CB} from the variations of I_B/I_C vs pressure in the low pressure regime. The analysis, which included an average radiative lifetime estimate for each electronic state, gave k_{CB} of 18, 17, 5.9, and 2.7×10^{-11} cm³ molecule⁻¹ sec⁻¹ for Kr, Ar, Ne, and He, respectively. Since the reaction of Cl, with Xe* gives a high vibrational distribution, these rate constants refer to $v \approx 100$. The I_B / I_C ratios from CCl₄ and COCl₂ do not increase as fast as for Cl₂; hence the transfer rate constants evidently are smaller for lower

TABLE I. XeCl energy levels and radiative lifetimes.

Vibrational	C state		B state			
level	Energy (cm ⁻¹)	τ (nsec)	Energy (cm ⁻¹)	τ (nsec)		
0	139.42	120.0	369.42	11.0		
4	876.08	127.6	1 136.05	11.08		
8	1 590, 86	136.4	1 882.33	11.88		
12	2 284, 25	137.2	2608.63	12.29		
16	2 956.77	142.8	3 315. 38	12.64		
20	3608,94	146.9	4 002, 98	12.53		
24	4241.29	152.3	4671.84	12.35		
28	4 854.33	174.1	5322.39	13.43		
32	5448.6	182.1	5955.05	14.10		
36	6 024, 61	195.3	6 570.25	14.50		
40	6 582.89	195.5	7168.42	14.84		
44	7 123.96	210.3	7750.00	16.12		
48	7648.33	224.6	8315.41	16.38		
52	8156.52	230.6	8 865.10	17.25		
56	8649.03	245.0	9399.49	18.69		
60	9126.35	256.4	9919.03	19.33		
64	9 588. 98	265.0	10424.17	20.15		
68	10 037.4	275.2	10915.27	21.35		
72	10472.1	279.1	11 392, 77	22.42		
76	10883.4	270.2	11897.07	23.88		
80	11 302.0	296.2	12308.67	24.78		
84	11698.1	298.2	12747.97	26.04		
88	12 082.3	308.3	13175.27	27.52		
92	12454.9	318.1	13 590. 97	28.98		
96	12815.3	325.6	13994.47	30.21		
100	13167	337.7	14389.17	31.77		
104	13507.3	343.3	14772.37	33.21		
108	13837.6	349.1	15145.174	35.14		
112	14158.1	352.8	15508.67	37.16		
116	14469.3	357.9	15862.27	39.03		
120	14771.5	375.1	16206.67	40.91		
124	15 065	398.5	16541.97			
128	15627.1	433.7	17186.47			
136	15896.2	438.5	17 496.07			

v levels. This is supported by the fact that the change in I_B/I_C "slows down" for higher pressure and in the intermediate regime (5-50 Torr of Ar) I_B/I_C is nearly constant. In this regime collisions with the *B* state become important and the slow change of I_B/I_C is due to a



FIG. 8. (a) Comparison of XeCl(B-X) experimental spectrum with two simulated spectra (--- and) which give satisfactory fits. The simulated spectra for the Cl_2 case are nearly superimposed. (b) Corresponding vibrational distributions.

combination of reduced transfer rate constants for the lower v levels and also to the balance in B and C state populations as the B-C transfer rate competes with radiative decay of the B state. At ~50 Torr the I_B/I_C attains its maximum value. Examination of the 10-100 Torr spectra indicates that the vibrational distributions are high temperature Boltzmann distributions, while the electronic state distribution is nonBoltzmann. By ~100 Torr, the vibrational distributions are nearly 300 °K. As the pressure is increased to the 1000 Torr region, the I_B/I_C ratio decreases as transfer between B and C occurs to give a Boltzmann electronic state distribution. At the highest pressures electronic transfer is complete, and interpreting the high pressure I_B/I_C ratio as a 300 °K distribution shows that the XeCl(C) state is ~ 200 cm⁻¹ lower in energy than the XeCl(B) state.⁷ The exact value of the energy separation is still being discussed. Tellinghusien and McKeever¹⁴(a) report a value of ~130 cm⁻¹ by interpreting the I_B/I_C high pressure intercept at 360 and 800 °K. (In addition, they were able to obtain $A_{C-A}/A_{B-X} \approx \tau_B/\tau_C$ of 0.087 which is in excellent agreement with the calculated value of 0,091.) Bokor and Rhodes, 14(b) on the other hand, report an energy separation of $\sim 5 \pm 25$ cm⁻¹ with the C state higher in energy. However, their experiments, which used an ArF laser to excite Xe/Cl_2 mixtures in Ar, extend to only 1000 Torr. In fact, pressures of ≥1000 Torr are required to obtain B/C equilibrium concentrations (see Fig. 2 of Ref. 7, for example). Thus the data of Bokor and Rhodes do not extend to sufficiently high pressure to obtain a true equilibrium I_B/I_C ratio. Experiments of the type described in Ref. 7 have recently been performed at low temperatures¹⁵ and preliminary results support an energy separation of ≈ 200 cm⁻¹. The uncertainty of the B-C energy separation does not affect interpretations of this paper because we are concerned with collisions of XeCl molecules in high-v levels.

III. METHOD FOR MODELING VIBRATIONAL RELAXATION AND *B-C* STATE TRANSFER

The method used to model the variation of the XeCl(B, C) vibrational distributions and B/C ratio as a function of pressure is essentially the same as the one used by Duewer, *et al.*¹⁶ in studying the rotational relaxation of CN(B, v=11). The one important difference here is the large variation in radiative lifetime which must be included in the calculation. Electronic quenching of XeCl(C, B) is assumed to be unimportant since the modeling only extends to 50 Torr. This approximation should be valid for all the bath gases studied except for

Xe. For XeF the quenching rate constants in the rare gases are typically $10^{-13}-10^{-14}$ cm³ molecule⁻¹ sec⁻¹ while the transfer rate constants are two orders of magnitude larger.¹³ No detailed modeling for XeCl in Xe will be presented because of the possible importance of electronic state quenching. The vibrational levels of XeCl(*B*, *C*) are divided into three ranges: low v(v = 0-30), mid v(v = 30-70), and high v(v = 70-130). Examination of Figs. 5-7 shows that Xe* + Cl₂ gives an initial vibrational distribution peaked at $v \sim 100$ with $\geq 80\%$ of the total in the high-v range; Xe* + CCl₄ gives an initial distribution peaked at $v \sim 50$ with 80% in the mid-v range, and COCl₂ gives a distribution peaked at v = 0 with 80% in the low-v range.

If the relative populations of XeCl(B, v) and XeCl(C, v) are considered to be a vector, then the normalized initial population vector X(0) is given by

$$X(0) = R_i / \sum R_i , \qquad (2)$$

where R_i is the formation rate into the *i*th level. If NC and NB are the maximum number of vibrational levels for XeCl(C) and XeCl(B), respectively, the total C and B populations are

$$N_{C} = \sum_{i=1}^{NC} X_{i}(0) \text{ and } N_{B} = \sum_{NC}^{NC+NB} X_{i}(0) .$$
 (3)

Since the reaction of Xe^{*} + Cl₂ populates levels up to v = 140 in the C state, X(0) would include over 200 levels if each vibrational level was included. To save computational time, the populations were grouped into every 4th vibrational level. The relative B to C formation rate is given by^{4(b)} the zero pressure I_B/I_C ratio, which was taken as 1.4 for all three donors from Fig. 4. The initial relative vibrational distribution within each electronic state was obtained from the simulation of the lowest pressure, typically ≤ 0.2 Torr, spectrum. The low pressure distributions shown in Fig. 5–7 are steady-state distributions and must be corrected for the lifetime variation to obtain the true initial distributions. ^{5(b)}

The relative populations that exist after exactly m collisions are given by

$$X(m) = \tilde{P}^m X(0) . \tag{4}$$

The transition matrix \tilde{P} , has elements P_{ij} which give the probability per collision with bath gas of a XeCl molecule in state j going to state i. \tilde{P} was partitioned into four parts as follows:

for $1 \le i \le NC$,	$1 \leq j \leq NC$,	$P_{ij}^{R} = C$ state relaxation ,	
for $1 \leq i \leq NC$,	$NC+1 \leq j \leq NC+NB$,	$P_{ij}^T = B$ to C transfer ,	
for $NC + 1 \leq i \leq NC + NB$,	$1 \leq j \leq NC$,	$P_{ij}^{T} = C$ to B transfer,	(5)
for $NC+1 \leq i \leq NC+NB$,	$NC+1 \leq j \leq NC+NB$,	$P_{ij}^{R} = B$ state relaxation .	

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IF

The diagonal elements of the matrix correspond to elastic collisions, which are unobservable in this case, and were calculated from the normalization condition

$$P_{jj} = 1 - \sum_{i} P_{ij} \quad i \neq j .$$
 (6)

By normalizing \tilde{P} in this manner, the sum of the inelastic and elastic rate processes is independent of vibrational level providing the collision frequency (cross section) is selected to be constant for all levels. In the modeling, the collision frequency was taken as a constant; but the ratio of the inelastic and elastic cross sections was allowed to be a function of vibrational level. The transition matrix is subject to detailed balance and up transitions were calculated from the model assumed for the down transitions, i.e., for j > i

$$P_{ji} = P_{ij} e^{-(B_j - B_i)/kT} . (7)$$

The probability that a molecule undergoes exactly m collisions before decaying by photon emission can be calculated as follows. For a molecule in a given level with a radiative lifetime τ , the distribution of times for radiative decay is given by

$$F(t) = \tau^{-1} e^{-t/\tau} . (8)$$

The fraction of molecules undergoing exactly m collisions in a fixed time interval t is given by

$$F(m) = \frac{(zt)^m}{m!} e^{-\pi t} , \qquad (9)$$

where z is the collision rate corresponding to a given pressure. The distribution for the number of collisions before radiative decay is given by the convolution of these two distributions over all time,

$$\mathbf{A}(m) = \int_{0}^{\infty} \tau^{-1} e^{-t/\tau} \frac{(zt)^{m}}{m l} e^{-zt}$$
$$= \frac{\tau^{-1}}{z + \tau^{-1}} \left(\frac{z}{z + \tau^{-1}}\right)^{m} .$$
(10)

This last quantity is the fraction of molecules undergoing emission after exactly m collisions but before the (m + 1)th collision. The emission intensity I from each level in the form of a vector is given by,

$$I = \sum_{m=0}^{\infty} \mathbf{A}(m) X(m)$$

$$= \sum_{m=0}^{\infty} \mathbf{A}(m) \tilde{P}^{m} X(0) ,$$
(11)

where A(m) is a vector and is different for each level because of the different values of τ_i . Although this equation contains an infinite number of terms, the summation can be approximated with a finite number of terms m^* because A(m) decreases with increasing m. In this work the summation was terminated when $\sum_i X_i(m^*)$ was $\leq 0.1\%$ of $X_i(0)$. For this criteria m^* usually ranged from 2 to 100 depending on pressure and bath gas. The intensity from individual levels is summed to obtain the I_B/I_C ratio. The intensities were converted to steadystate concentrations $X_i(s)$ by

$$X_i(s) = I_i \tau_i . \tag{12}$$

If lifetimes for all levels were equal, the relative steady-state concentrations and intensities would be equivalent and no conversion would be needed. The distributions given by $X_i(s)$ are compared to the distributions obtained from simulation of the experimental spectra at a given pressure to gain information about the form of P_{ij} .

Assignment of the model for \tilde{P} was based on a trial and error approach. We began with simple models and added more flexibility as necessary. We wanted overall rate constants for transfer and vibrational relaxation, as well as state-to-state rate constants. The state-tostate processes are determined by the form of $ilde{P}$ and the rate constants for total removal of level j by $z \sum_{i} P_{ij}$ $(i \neq j)$. The success of a model for \tilde{P} is judged by how well the calculated distributions fit the variation of the shape of the simulated distributions with change in pressure. On the other hand, the rate of relaxation of the vibrational distributions as a function of pressure depends on both the collision rate z (or σ , the total collision cross section) and \tilde{P} . Because it was not possible to determine the magnitude of the elastic cross section from our data, the selection of the total cross section is somewhat arbitrary. For our purposes the only restriction on σ is that it be large enough to give the required rates of relaxation and transfer. Initially, we estimated "reasonable" values for the collision cross section and proceeded with the modeling. But in some cases it was subsequently necessary to increase σ because the required rates of relaxation and transfer could not be made fast enough for the first choice for σ . After selection of a \tilde{P} that fitted the overall shape of the distributions, though not necessarily at the right pressures, the inelastic cross section could be increased or decreased until the distributions matched at the proper pressure.

The objective is to obtain a model for the transition matrix \tilde{P} which simultaneously fits all of the experimental data, i.e., the B and C distributions and the $I_{\rm B}$ I_c ratio as a function of pressure for all three Cl donors. Preferably the model should be described by as few independent parameters as possible. Calculations were first done for XeCl in Ar. Relaxation and transfer are both sufficiently fast that changes occur at relatively low pressure. Since the required number of iterations needed for convergence depends on pressure, analysis of the argon data for a given degree of relaxation requires less computer time than for He or Ne. The fitting for Ar also provides a good reference point for both lighter and heavier bath gases. To aid in the discussion and in identification of results, each model will be given a label (capital letter) as it is presented. Several different models were tried. Each of these models has several parameters which can be varied, but we present only the best set of parameters from the several trial and error attempts to obtain a satisfactory fit to the experimental data. Table II contains a summary of the models and the collision cross sections.

4367

TABLE II. Rate constant summary.

Bath gas	Model parameters					k _R ⁴							
	Model	ь	С	F	Rib	T ₁ ^b	D°	low v^d	mid v	high v	low v^d	mid v	high v
Ar	A	0,11	•••	•••	•••	•••	4,95	4.5-13	13-20	20-34			<u> </u>
	B	0,10	0.10	0,15	1.0	1.2	6,0	2.5-13	13-25	25-35	3.0-11	11-15	15-15
	С	0,15	0.2	0.15	0.5	1.2	6.0	1.0-6	6.0-12	•••	3.0-11	11.0-15	•••
He	D	0,3	0.2	0.10	0.11	0.15	4.0	0,15-1,1	1.1-2.5	2,5-4,4	0,5-1,8	1,8-2,5	2, 5-2, 5
Ne	E	0.2	0,15	0,13	0.3	0.3	5.0	0.5-2.9	2.9-6.2	6,2-9,5	0.7-2.6	2.6-3.5	3.5-3.5
Kr	F	0.05	0.05	0,20	0.2	1.1	7.0	0.6-7.7	2.7-5.5	5.5-7.3	3.0-11	11.0-16	16-16
Xe													~ 15-20

^aUnits of 10⁻¹¹ cm³ molecule⁻¹ sec⁻¹; the k_T in this table take precedence over all other previous reports in Refs. 5(b) and 7. R_2-R_4 and T_2-T_4 were the same for all models. $R_2-R_4=0.1$, 1.0, -0.3 and $T_2-T_4=0.1$, 0.7, -0.5.

^eCollision diameter in angstroms used to calculate the collision frequency.

^dThe low, mid, and high v represent the ranges v = 0-30, 30-70, and 70-130, respectively.

IV. RELAXATION IN ARGON

A. Vibrational relaxation of XeCl (C, high v)-Model A

The XeCl(B) radiative lifetime is less than the time between collisions for pressures ≤ 2 Torr, and B to C transfer cannot be important in this range. Therefore the change in the XeCl(C) distribution is solely due to vibrational relaxation. Although this statement is qualitatively correct, 20% of the XeCl(B, v = 100) molecules undergo at least one collision at 0.5 Torr. This percentage increases to 40% at 1 Torr and ~55% at 2 Torr; but, as a first approximation, B to C transfer can be ignored and C state relaxation can be modeled as vibrational relaxation for pressures ≤ 2 Torr.

The initial model used to calculate the transition matrix elements P_{ij}^{R} for transitions j > i was given by

$$P_{ij}^{R} = a \left[\frac{kT}{\Delta E} + \exp\left(-\frac{b\Delta E}{kT}\right) \right], \qquad (13)$$

with $\Delta E = E_i - E_i$. The constants *a* and *b* were treated as adjustable parameters and were varied to obtain a satisfactory fit to the data. The kT factor (k = Boltz - boltzmann constant and T = 300 °K) serves to make ΔE unitless and has no other physical significance. For some values of a and b, $\sum_{i\neq j} P_{ij}^{R}$ was greater than 1 and values of P_{ij}^{R} calculated by the above equation were multiplied by a normalization constant so that $\sum_{i} P_{ii}^{R} = 1$. Certain variations of the above model also were explored; P_{ij}^{R} $=a + \exp(-b\Delta E/T)$, $P_{ij}^{R} = akT/\Delta E$, and $P_{ij}^{R} = \exp(-b\Delta E/T)$ T), and close fits were obtained for most of these variations. However, the "best" overall fit was obtained with Eq. (13) for a = 0.05 and b = 0.11. The dominant contribution to the magnitude of P_{ij}^{R} is given by the exponential term and since the vibrational relaxation could be fitted satisfactorily with just an exponential term, ¹⁷ the other models presented later do not include the $kT/\Delta E$ term.

The population distributions resulting from model A are compared in Fig. 9 to the simulated distributions at several pressures. The fit is well within the 10% uncertainty of the experimental distributions throughout

the 0.11 to 2.2 Torr range. Note especially the good fit for P=2.2 Torr for $20 \le v \le 110$. By combining the collision frequency and the $\sum_i P_{ij}$ values, the relaxation rate constants $k_R(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \sec^{-1})$ as a function of v level are 4.5-13, 13-20, and 20-35 for v=4-30, 30-70, and 70-130, respectively. The smooth increase of the rate constants with v is due to the smaller energy separation between high-v levels and the larger number of levels below a given v level.

For model A the P_{ij}^{R} decline smoothly with increasing ΔE . Single level jumps (which for our model include all transitions from v to v-1, v-2, v-3, and v-4) are the most important; however, multilevel transitions also are significant. The adjustable parameter b in the exponential term governs the range of ΔE . For small b, the low-v range gains in population at the expense of the high v and the distribution is broadened, whereas for larger b the distribution remains sharp and moves systematically to lower v. For a successful fit b must be 0.1-0.2. The success of this model is due to the fact that molecules in the high-v range (v=70-130)



FIG. 9. Comparison of simulated distributions (----) and calculated distributions from Model A (---) for the vibrational relaxation of XeCl(C) in Ar.

have a significant probability of transfer to the low-v range (v = 4-30). This must be a general feature of all models that fit the relaxation of XeCl(high v) in Ar.

Since the distribution from $Xe^* + Cl_2$ is in the high-vrange, the model should be most reliable for these levels. Most of the population in the low-v levels from $Xe^* + Cl_2$ arises from multiple collisions and the model may not be very reliable for the transition probabilities of the lower levels.

B. Vibrational relaxation and transfer of XeCI (high ν)---Model B

Before proceeding with the addition of the XeCl(B) state to the calculations, certain assumptions must be made. Because C to B transfer is an important process at low pressure, apparent vibrational relaxation of B observed before bath gas collisions with B are important. At higher pressures, where XeCl(B) + bath gas collisions become important, the vibrational distribution of XeCl(B) has relaxed so much that obtaining information about XeCl(B) vibrational relaxation is impossible. Without any knowledge to the contrary, we will assume that B state relaxation can be described by the same model as for XeCl(C). We will drop the $kT/\Delta E$ term because of its minor role, and the model for vibrational relaxation becomes

$$P_{ij}^{R} = \exp(-b\Delta E/kT) . \tag{14}$$

Since the vibrational levels of (C) are closer together than for (B), the $k_R(B)$ are slightly smaller, typically by 10-20%, than $k_R(C)$ for the same v level.

The additional assumption concerns B - C transfer. A P_{ij}^T model developed for $C \rightarrow B$ excergic transitions would give the reverse (endoergic) $B \rightarrow C$ transitions by microscopic reversibility. However, a model is also needed for the B - C excergic transitions. For the same reasons as given above, reliable information for this $B \rightarrow C$ transfer, particularly from XeCl(B, high v), is not available. However, detailed balance can be used to relate the forward and reverse B-C transfer rates, and, limiting high temperature, the forward and reverse rates would be equal. Although the translational temperature is near 300 °K, it is reasonable to assume that for high vibrational excitation, $k_{BC}(E'_v) \approx k_{CB}(E_v)$, where $E_{v}^{\prime}\approx E_{v}$, and that the form for P_{ij}^{T} is the same for both XeCl(B) and XeCl(C). The XeCl(C, v=0) level, which represents the total v = 0-3 population) is the lowest level and has no down transition, hence its k_T and P_{ij} values are determined completely from detailed balance. The course graining will result in an increasingly erroneous representation as the XeCl population builds up in the lowest levels of B and C.

In contrast to modeling the C state vibrational relaxation, simultaneous fitting of the B and C distributions and the I_B/I_C ratio as a function of pressure was extremely difficult. Considerable effort was expended in obtaining a model that was sufficiently flexible. We initially used the same form for P_{ii}^{T} that was used for vibrational relaxation and varied the parameters, as well as the relative importance of transfer vs relaxation. For a given C level the highest transfer probability will be to the adjacent lower B level, according to this model. For certain values of the parameters, the I_B / I_C ratio could be matched (and also C state vibrational relaxation), but the B state vibrational distribution was always too high in energy. An additional problem arose because the energy difference between adjacent B and C levels (note, our calculation uses every fourth real level) was not constant with v, because the values of ω_e and $\omega_e x_e$ for XeCl(B) and XeCl(C) differ and the calculation gave P_{ij}^{T} of widely varying magnitude for adjacent levels, which led to spikes in the B distribution which were difficult to compare with the smooth simulated distributions. Improvements were necessary to rectify these problems.

The final model adopted for P_{ij}^T requires that the most probable transition from a given j be to the energy region E_0 and has the following form:

$$P_{ij}^{T} = \frac{kT}{C} \int_{B_i}^{B_{i+1}} \exp(-C \cdot E^*/kT) dE^* ,$$

$$E^* = \left| \Delta E - E_0 \right| , \qquad (15)$$

where kT and ΔE are defined as before, C is the adjustable parameter, and E_0 is given by

$$E_0 = (1.0 - F \cdot E'_j) E_j \,\mathrm{cm}^{-1} \,. \tag{16}$$

In Eq. (16) $E'_{j} = E_{j} / 16000 \text{ cm}^{-1}$ (16000 cm⁻¹ is approximately the energy of the highest populated levels in the $Xe + Cl_2$ reaction) and F is an adjustable parameter. Eq. (15) allows the most probable transfer to be fixed at E_0 , with E_0 being some fraction of initial energy. With the benefit of hindsight, the $E_j/16000 \text{ cm}^{-1} \text{ term}$ was added so that the lower v levels would lose less energy than higher v levels. The use of the integral in Eq. (15) eliminates the computational artifact of widely varying P_{ii}^{T} for adjacent levels and gives smooth steady-state B distributions. However, the integral also gave nearly constant $\sum_{i} P_{ij}^{T}$ values, which are independent of j, and hence the k_T are independent of vibrational level. To regain the ability to control the magnitudes of k_T for different v levels the $\sum_{i} P_{ij}^{T}$ values were fixed by a series expansion

$$\sum_{i < j} P_{ij}^{T} = T_1 (T_2 + T_3 E_j' + T_4 E_j'^2) , \qquad (17)$$

where T_i are adjustable parameters. To increase flexibility, a similar expression was used for $\sum P_{ij}^R$:

$$\sum_{i < j} P_{ij}^{R} = R_1 (R_2 + R_3 E'_j + R_4 E'_j^2) , \qquad (18)$$

with R_i adjustable. The factors R_1 and T_1 allow the magnitude of k_T and k_R to be altered by changing the ratio of elastic and inelastic components of the cross section. The parameters $R_2 - R_4$ and $T_2 - T_4$ provide the functional dependence of $\sum_i P_{ij}$ on v level. The most ex-



FIG. 10. Comparison of simulated (--) and calculated distributions from Model B (--) of XeCl(B) and XeCl(C) from Xe*+Cl₂ in Ar. Model B includes both relaxation and transfer processes. The apparent populations in the lowest two levels, which represent the real v = 0-8 levels for the higher pressures, cannot be interpreted literally (see text).

tensive experimental data exist for Ar as the bath gas. For this reason $R_2 - R_4$ and $T_2 - T_4$ were established for Ar and were not changed for the other bath gases. Several calculations were done to determine a good set of parameters. Model B was chosen as giving the best fit to the $Xe^* + Cl_2$ data. The parameters for Model B are b = C = 0.1; f = 0.15; $T_i = 1.2$, 0.01, 0.7, and -0.5; and $R_i = 0.1$, 0.01, 1.0, and -0.3 for i = 1, 2, 3, and 4, respectively. The calculated results are compared to the experimental distributions and I_B/I_C ratios in Figs. 10 and 11. The fit is fairly good for the B-state distribution. The fit to the C-state distributions, while not as good as for Model A, is still within the uncertainty of the distributions and there is no point in trying to improve them. The I_B/I_C fit is excellent below ~ 5 Torr and is only slightly lower for the higher pressures. In fact, the calculated I_B/I_C ratio begins to decrease at 8 Torr while for experimental points continue to rise. This suggests that the transfer rate constants for the lower v levels are too low relative to the high-v levels and/or that the C state is vibrationally relaxing too fast. In either case, as the C-state population builds up in low levels, the C to B transfer slows down with increasing pressure. The second reason is substantiated by the 8.0 Torr results of Fig. 10, which show that the calculated populations are too high in the low-v range where the C-B transfer rate constants are the smallest. Since the calculations match lower pressure data where the distribution is largely above v = 70, this model was considered successful in fitting the $Xe^* + Cl_2$ data. In the next section Model B is modified slightly to give a good fit to the $Xe^* + CCl_4$ data with a distribution that initially is in the mid-v range and the question concerning the relaxation and transfer rates for v = 30 - 70 will be addressed then.

Combination of the transition probability matrix ele-

FIG. 11. Comparison of experimental and calculated I_B/I_C ratios in Ar. For clarity the I_B/I_C ratios have been moved up 4 and 2 units for Cl_2 and CCl_4 , respectively. The calculated results are the dashed lines (best fit) or dotted line. The best-fit results are from Model B for Cl_2 and Model C for CCl_4 and $COCl_2$. The dotted line is a Model B calculation for CCl_4 ; the poor fit necessitated an improvement and led to Model C.



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP



FIG. 12. Comparison of Model B (•••) and Model C (---) results for Xe*+CCl₄ data. The poor fit for Model B required improvement and Model C was developed to fit the Xe*+CCl₄ data (see text).

ments with the collision frequency gives the rate constants listed in Table II. The relaxation rate constants agree favorably with the results from Model A. The k_R calculated here are slightly larger than for Model A and, as discussed above, may be too large for the low-and mid-v range. Nevertheless, the good fit to the data suggest that the k_R for the high-v range are $(20-35) \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹. The good fit to the *B*-state distribution and the I_B/I_C ratio below 5 Torr suggests that the k_T are also reliable, at least for high-v levels. The form of P_{ij}^R was discussed when Model A was presented and the results for Model B are very similar (see Fig. 13); however, the form of P_{ij}^T differs from P_{ij}^R . The C molecules enter the B state in an energy range that is peaked at ~ 10% -15% below the initial energy level.

C. Relaxation and transfer of XeCl (mid v) and XeCl (low v)-Model C

Since a satisfactory fit was provided to the Xe^{*} + Cl₂ data, Model B was used to examine the data from the Xe^{*} + CCl₄ reaction, which emphasizes the mid-v range. The results are shown in Fig. 12 for three pressures and, as can be seen, the B and C states both relax too fast and I_B/I_C increases too slowly with increasing pressure (Fig. 11). The following improvements are needed. Since XeCl(C) relaxes too fast, $k_R(v=30-70)$ should be reduced. The low I_B/I_C could be a consequence of the (too) fast relaxation of the C state and/or k_T being too small for v = 30 - 70. Since the B state also relaxes too quickly, k_r probably is too large or transfer occurs with too large a loss of energy. The most probable energy loss by transfer of molecules from C(v=50) to B(v) is only 7-8% of the initial energy and further reduction of this will not give much improvement. Hence, the best way to simultaneously reduce the rate of B-state relaxation and increase the I_B/I_C ratio is to increase the C parameter in Eq. (16); this gives a sharper v-level distribution entering the B state. In addition, decreasing $k_{\rm R}$ to fit the C relaxation will increase $I_{\rm B}/I_{\rm C}$. The following modifications to Model B were made: R_1 was changed to 0.50 which reduced k_R by a factor of ~2; the parameter C is Eq. (15) was changed to 0.2 which reduced the B-state relaxation rate, and b was increased to 0.15, which gave a slightly better fit than using b = 0.10. The rest of the parameters were the same as for Model B. The results from this calculation. hereafter denoted as Model C, are compared in Figs. 11 and 12 and the fit is seen to be much improved. The calculated transfer rate constants for Model C are the same as for Model B and the only difference is the form of P_{ii}^{T} . The relaxation rate constants for Model C are 1.0-6.0 and $6.0-12 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹ for the low-v and mid-v range, respectively. The results for low v are less reliable than for mid v because low-v levels are populated by multiple collisions. The Model C rate constants, which are approximately half the values from Model B, should be more reliable because (i) the fit to the CCl₄ results are better, and (ii) the effect of multiple collisions is less severe in the mid- and low-vrange for the CCl_4 data than for the Cl_2 data.

Model C was used to examine the Xe^{*} + COCl₂ data. The fit to the I_B/I_C data shown in Fig. 11, though not as good as for the other two reactions, is satisfactory. The distributions based on simulation of the Xe^{*} + COCl₂ spectra are only qualitatively reliable because lack of oscillatory structure in the spectra prevents reliable assignment of the vibrational distributions. Nevertheless, Model C does give acceptable results and no attempt was made to further improve the model for the low v regime.

V. RELAXATION AND TRANSFER IN OTHER BATH GASES

A. XeCl (high v) in helium and neon

In this section we extend the model to include other bath gases. For the most part these results are based on the Xe^{*} + Cl₂ reaction and will be strictly valid only for XeCl high v. Only the final results will be stated. Examples of the results of the simulation and modeling results for these gases, such as shown in Figs. 1-3 and 10-12 for Ar, can be found elsewhere.¹⁸

Inspection of the I_B/I_C ratios [Fig. 4(b)] for XeCl in He and Ne indicates that transfer is much slower in these bath gases than in Ar. In addition, the XeCl(B, C) vibrational distributions relax much slower in He and Ne than in Ar. For example, at 30 Torr of He the distributions are less relaxed than at 2 Torr of Ar. Before discussing the He and Ne results, it is necessary to make a few comments concerning the deduction of $P_{i,i}^{R}$ For the Ar case, sufficient changes in the vibrational distributions occur at rather low pressures so that the effects of just a few collisions with the bath gas can be observed and the P_{ij}^{R} elements can be assigned with some confidence, i.e., the parameter b was determined with some reliability. For He or Ne, on the other hand, pressures of 10-20 Torr are required to see significant changes in the distributions, and small changes in energy with large cross sections are difficult to distinguish from larger changes with smaller cross sections. It is impossible to simultaneously determine P_{ij}^{R} and the inelastic collision cross section with reliability. For C-B transfer this situation is alleviated because the I_B/I_C ratio identified the cross section (or magnitude of k_T), and the model for P_{ij}^T can be determined more reliably.

For He and Ne we used the same general form for P_{ij}^T and P_{ij}^{R} as for the Ar case and varied the parameters until a successful fit to the data was found. The best transfer model for He was with C = 0.2, f = 0.9, $T_i = 0.15$ with $T_2 - T_4$ the same as for Model C, and a collision diameter of 4 Å. This gave k_T of 0.5-1.8, 1.8-2.5, and $2.5-2.5\times10^{-11}$ cm³ molecule⁻¹ sec⁻¹ for the low-, mid-, and high-v ranges, respectively. For vibrational relaxation a range of parameters could be used with nearly equal success. For example, with R_2-R_4 the same as for Model C, successful fits were obtained with b = 0.1 - 0.5 and $R_1 = 0.05 - 0.2$. However, the best overall fit was judged to be for b = 0.3 and $R_1 = 0.11$, and these values were adopted for the best fit to the He data. These gave $k_R = 0.15 - 1.1$, 1.1-2.5, and 2.5-4.4×10⁻¹¹ cm^3 molecule⁻¹ sec⁻¹ for the low-, mid-, and high-v ranges, respectively.

The neon results were much the same as for He. Relaxation again cannot be determined accurately and several models could fit the experimental results satisfactorily. The best model (E) used $R_i = 0.3$, 0.01, and 1.0-0.3; $T_i = 0.3$, 0.01, 0.7, and -0.5 for i = 1-4; and b = 0.2, c = 0.15, and d = 0.87, with a collision diameter of 5 Å. These parameters gave $k_T = 0.73-2.6$, 2.6– 3.5, and $3.5-3.5 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹ and k_R = 0.48-2.9, 2.9–6.2, and $6.2-9.5 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹ for the low-, mid-, and high-v ranges, respectively.

B. XeCl (high v) in krypton, xenon, and nitrogen

In these bath gases the relaxation and transfer rates are faster than in Ar. The simulated distributions could be represented by a high temperature Boltzmann distribution at pressures as low as ~5 Torr. The problems encountered in assigning the relaxation rate constants for He and Ne are not present here because significant changes in the distributions are observed below 1 Torr and both P_{ij}^{R} and P_{ij}^{R} can be assigned in a straightforward way. For Kr we used the same model that was developed for the argon case. The best parameters are b = 0.5, c = 0.5, and f = 0.8; $R_i = 0.2$, 0.01, 1.0, and 0.3; and $T_i = 1.1, 0.1, 0.7, and -0.5$ for i = 1-4, with a collision diameter of 7 Å. These gave $k_R = 0.6 - 2.7, 2.7 - 5.5$, and 5.5-7.3×10⁻¹¹ cm³ molecule⁻¹ sec⁻¹ and $k_T = 2.9 - 10^{-11}$ 11.0, 11.0-15.5, and $15.5-15.5\times10^{-11}$ cm³ molecule⁻¹ sec^{-1} for the low-, mid-, and high-v ranges. The Kr transfer rate constants are only slightly larger than for Ar which is consistent with the I_B/I_C ratios in Fig. 4(b). However, the relaxation rate constants are significantly smaller than for Ar and, in fact, are even less than for Ne. Yet the observed overall rate of vibrational relaxation is faster in Kr than in Ar because more vibrational energy is lost per collision. Efforts were made to use a model with smaller loss of energy and larger k_R to fit the Kr results but the fit to the simulated distributions was not as good as for Model F.

Xenon data could not be obtained using the flowing afterglow or resonance absorption method because these methods fail for high Xe pressures. Instead, XeCl* emission was obtained in the presence of Xe bath gas by flowing a ~ 1% Cl₂ mixture in Xe through a pulsed discharge and observing the XeCl* emission directly in the discharge; the details will be reported elsewhere.¹⁹ This method is not specific in the excitation mechanism; i.e., XeCl* formation may result from Xe(6s) and Xe** Rydberg state atoms reacting with Cl_2 or possibly even ion-ion combination. Furthermore, changing the Xe pressure may alter the distribution of excitation mechanisms. Preliminary interpretations¹⁹ indicate that the reaction of Cl₂ with Xe** Rydberg states is an important mechanism for the discharge source because the inital vibrational distribution is much broader than the one from the $Xe({}^{3}P_{2})$ reactions. Although a detailed analysis of the vibrational relaxation and transfer in Xe will have to await a fuller understanding of the excitation mechanism, we estimate from the I_B/I_C in Fig. 4(b) that k_T $\sim 15-20 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \text{ for XeCl (high } v)$ +Xe. The vibrational relaxation resembles the Kr case with (possibly) even more vibrational energy lost per collisions.

Because N_2 also quenches $Xe({}^{3}P_1)$, the quality of the experimental data for XeCl* in N_2 was poor and no detailed calculations were performed. However, the appearance of the spectra as a function of N_2 pressure closely resembles the Kr bath gas case. The I_B/I_C ratio [Fig. 4(b)] is also similar to Kr. Although no quantitative results can be given, it appears that the magnitude of the rate constants and the form of \tilde{P} for N_2 should be quite similar to that for Kr.

VI. DISCUSSION

A. Reliability of rate constants and models

Before interpreting our results in terms of molecular interactions, it is necessary to assess their accuracy. There are several factors affecting the magnitudes of the rate constants. While there may be some uncertainty in the populations associated with the assumed potentials and dipole moment function, they should be small on a relative basis because all spectra were simulated using the same assumptions. In addition, the simulation of the B-X spectra was straightforward because the X potential is nearly flat in the Franck-Condon region. While the vibrational distribution gives the spacing and amplitude of the oscillating structure, the overall intensity distribution of the experimental spectra is governed by the dipole moment function, which could be determined reliably.^{5(b)} Another possible factor could be our neglect of the B-A transition which overlaps the C-A emission. As a result, the B-A and C-A would have to be deconvoluted to obtain the true C-A emission. However, there is no systematic way to do this and the overall change of the emission as the pressure is increased is not large enough to warrant this correction. A more important consequence of correcting for the B-A is the increased I_B/I_C values implying larger k_T for XeCl (C, high v). Using the two-state model^{4(a),7} discussed earlier, calculations were performed to derive k_T based on the corrected I_B/I_C plots. In all cases the k_T increased by 30%-50%. However, the two-state model requires values for the lifetimes of both the B and C states and the original k_{τ} could be recovered with a similar adjustment of the lifetimes. Based on these results, we conclude that the most important variable affecting the magnitude of the rate constants is the lifetimes used in the calculations. Since these are only good to $\sim 30\%$ and since the population distributions are uncertain to $\pm 10\%$, the magnitude of the rate constants are no better than $\pm 40\%$ on an absolute basis. The relative values should be better than this. In general, the k_T should be more reliable than k_R for two reasons: (1) the experimental $I_{\rm B}/I_{\rm C}$ defines the magnitude of $k_{\rm T}$ (subject to the above-mentioned qualification), and (2) the simulated distributions of the B state are more reliable than for the C state. Thus modeling the B-state distribution while simultaneously fitting the I_B/I_C ratio in the low pressure regime provides a reliable estimate for k_T (high v). Of course, relaxation and transfer are not independent and, since k_T depends on vibrational level, the rate at which C relaxes will have an effect on the rate of transfer. This was noted previously with Model B, which overestimated k_R in the mid-v range, causing fast vibrational relaxation and, consequently, the transfer rate decreased too quickly. Nevertheless, the ~40% estimate should provide a reliable limit to the accuracy of our results for k_T and k_R . The values for k_T (high v) deduced from modeling agree favorably with the estimates from a two-state model (Sec. II) affirming that the high-vlevel assignments must be reasonably reliable.

With the above comments in mind, a glance at Table II reveals the following points:

(1) The k_T increase in the order He < Ne < Ar < Kr < N₂ ~ Xe.

(2) The k_R increase in the same order except for Kr (and possibly Xe).

(3) Both k_R and k_T depend on vibrational level, increasing in magnitude with increasing v.

(4) The sum of $k_R + k_T$ is nearly gas kinetic in magnitude for the high v.

FIG. 13. Comparison of relative $z \cdot P_{ij}$ for Models A and B for starting v = 20, 40, and 108. $\bullet = z P_{ij}^R$ (Model A), $\bullet = z P_{ij}^R$ (Model B), and $* = z P_{ij}^T$ (Model B).

(5) As the bath gas becomes heavier, k_T becomes increasingly important relative to k_R and dominates for Kr (and Xe?). Figure 13 shows a plot of $z P_{ij}^R$ (stateto-state rate constants) vs ΔE for Model A, $z P_{ij}^R$ and $z P_{ij}^T$ for models B and C for v = 108, 60, and 20. For v = 108, the magnitude of P_{ij}^R is similar for models A and B. The slight difference in shape is due to the inclusion of the $1/\Delta E$ term in Model A.

Because of the large number of vibrational levels and multiple collisions involved in a steady-state system, unique solutions to P_{ij}^{R} and P_{ij}^{T} are not possible. However, the models we developed for P_{ij}^{T} and P_{ij}^{R} are useful for contrasting the relaxation and transfer in the various bath gases. Time-resolved studies would be required to obtain better transition probability matrices.

It is evident from Fig. 13 that the mean energy loss per transfer collision is greater than for relaxation; however, the variation of P_{ij}^T with ΔE is nearly the same as P_{ij}^R for $\Delta E \ge 0.15 E_j$. An exponential gap model could not be used to fit transfer. For $\Delta E \le E_j$ it was necessary to reduce the transfer in this ΔE range so that the *B* vibrational distribution would relax fast enough and still match the I_B/I_C ratio. However, the bulk of the transfer takes place with ΔE similar to relaxation.

In Fig. 14 the difference in P_{ij}^{R} and P_{ij}^{T} for He and Kr are contrasted. As can be seen, the results are quite different for the two bath gases. Both transfer and relaxation in Kr involve loss of large amounts of vibrational energy and significant probability for large quantum





FIG. 14. Comparison of P_{ij}^{T} (upper panel) and P_{ij}^{R} (lower) for He (Model D) and Kr (Model F) as bath gases. To emphasize the differences between the two models, the maximum P_{ij} have been normalized to 10.

transitions. In He the P_{ij}^{R} and P_{ij}^{T} are grouped more sharply around the initial level. Both Ne and Ar lie between the extremes for He and Kr.

B. Interpretations of models

Before discussion of rare gas-XeCl interaction potentials, our results will be compared with pertinent data in the literature. Most studies of vibrational relaxation in diatomic molecules have focused on low vibrational levels where the spacing between levels ΔE is greater than kT. In the present case, the inelastic cross sections are large and the $\Delta E < kT$. For this reason we compare our results with vibrational deactivation of KBr[†] († represents vibrational excitation) formed from K+Br₂. The relaxation of KBr seems an ideal choice for several reasons: (1) reaction of $Xe^* + Cl_2$ is in many ways⁵ similar to K+Br₂ and both XeCl* and KBr have $\langle E_{\nu} \rangle$ of ~40 kcal mole⁻¹; (2) both KBr and XeCl^{*} are ionic in nature; and (3) an extensive amount of work has been reported on the vibrational deactivation of KBr. Fisk and co-workers studied KBr relaxation via observation of inelastic scattering of KBr for several collision partners.²⁰ In addition, both trajectory studies of KBr

+ Ar^{21} vibrational relaxation and an information theoretic analysis of experimental data have been reported.²² We first compare our results with their data by the information theoretic approach. Since KBr was studied by beam techniques, the experimental data consist of the flux density of scattered KBr as a function of center of mass scattering angle and relative velocity.²⁰ The information theoretic analysis of Crim and Fisk²² compared the measured translational energy distribution $P(f_T)$, where f_T is the fraction of initial energy appearing as product translational energy, with a prior of reference distribution $P^{\circ}(f_T)$. The appropriate prior for diatomicatomic collisions in the rigid rotor-harmonic oscillator limit is

$$P^{\circ}(f_{T}) = A_{T} f_{T}^{1/2} (1 - f_{T}) , \qquad (19)$$

where A_T is a normalization constant.

Apparently $P(f_T)$ was obtained by averaging over the experimentally observed center of mass angular range $(\sim 45^{\circ}-80^{\circ})$.²² Since there is a significant correlation between the scattering angle and the KBr translational velocity distribution, these "average" experimental distributions may not be good representations of the total distribution. However, the reported distributions are clearly two component with one component (the larger) centered around the elastic limit and the second centered around a large inelastic transfer. These two components give two linear regions on the surprisal plot.²²

To facilitate the comparison, we give our results in a similar manner. Because the initial internal energy of XeCl* is large $(E_{mp} \sim 40 \text{ kcal/mole for Xe}^* + \text{Cl}_2)$, the total energy of the rare gas +XeCl* collision is approximately fixed. Furthermore, if vibrational to translational inelasticity is the dominant deactivation mechanism, f_T for P_{ij} is given by

$$f_T = \frac{E_i - E_i}{E_j + kT} \quad . \tag{20}$$

The distributions $P(f_T)$ and $P^{\circ}(f_T)$ for various bath gases are shown in Fig. 15 for XeCl (v = 100) along with the surprisal $I(f_T)$

$$I(f_{T}) = -\ln \left[P(f_{T}) / P^{\circ}(f_{T}) \right] .$$
(21)

If the surprisal is linear, the departure of $P(f_T)$ from $P^{\circ}(f_T)$ can be described by a parameter λ , where $\lambda = dI(f_T)/d(f_T)$.

If $\lambda = 0$, relaxation takes place statistically while a positive or negative λ indicates relaxation occurs with transfer of less or more than the statistical amount of energy, respectively. As can be seen from Fig. 15, the surprisals are linear for He and Ne but deviate from linearity for Ar and Kr. However, a linear plot can be forced and the λ values given in Table III range from 17.6 for He to 1.5 for Kr. In Fig. 13 it was shown that Models A and B predict P_{ij}^R which deviate slightly from each other. This deviation is largest for large ΔE transitions (i.e., large f_T) and, consequently, the surprisals shown in Fig. 15 should be regarded as uncertain in this region. Hence the linear surprisal parameters were obtained only from points with $f_T < 0.7$. All of the surprisals show a marked difference (positive deviation)



FIG. 15. Comparison of translational energy distributions $P(f_T)$ (-----) (lower) and the corresponding surprisals (upper), calculated from Eq. (21) for the various bath gases. Because the calculations included only every fourth level, the origin of f_T is 0.05.

from the statistical case. A similar analysis for P_{ij}^{T} gave the same qualitative trends for the bath gases but with λ reduced by a factor of ~2 relative to P_{ij}^{R} . The large positive λ for He indicates collisions with XeCl* are nearly elastic, i.e., little energy is transferred from XeCl* into translation. Collisions with Kr, however, distribute large amounts of initial vibrational energy into translation and bring about rapid equilibration of translational and internal degrees of freedom. Although modeling was not attempted for Xe as the bath gas, the trends evident in Table III would predict that Xe-XeCl* collisions bring about a statistical or near-statistical exchange of energy.

The results of the surprisal analysis are contrasted in Table III with the results of vibrational relaxation of KBr. As already noted, Crim and Fisk²² found two linear regions in their surprisal plot for inelastic scattering of KBr. The component at low f_T gave a large λ consistent with nearly-elastic scattering and the f_T > 0.2 component gave $\lambda \sim 0$ which corresponds to nearlystatistical redistribution of energy. The $I(f_T)$ in Fig. 15 for Ar and Kr also *could be approximated* by a twocomponent distribution similar to that found for KBr. The distributions of Crim and Fisk strongly resemble the sum of an exponential $P_{ij} \propto \exp(-\Delta E_{ij}/b)$ and linear $P_{ij} \propto a \Delta E_{ij}$ distribution. However, theirs is a much more extreme form than our Model A. We must conclude that, although the two transition probability models are qualitatively similar, they differ significantly at the quantitative level. This disagreement could be a consequence of the lack of inclusion of all scattering angles in the beam studies, the difficult in obtaining single collision transition probabilities from our steady-state experiments, or a real difference as a consequence of the different intermolecular potentials (see next section) for KBr and XeCl + rare gas.

Included in Table III are the mean energy loss collisions for XeCl relaxation and transfer and for KBr relaxation. For Ar and Kr, the $\langle \Delta E \rangle$ for XeCl is the order observed for KBr deactivation. However, Ne appears to deactivate KBr much more efficiently than XeCl*. In fact, Ne appears to deactivate KBr more efficiently than Ar, which is contrary to what one would expect. Simple theory as well as experimental evidence indicates that for efficient coupling, the collision time and the vibrational period of the oscillator should be closely matched. For light molecules in low vibrational levels with large vibrational frequencies, this results in lighter gases, e.g., He, being more efficient for vibrational relaxation. For KBr or XeCl* in high vibrational levels, the oscillator frequency is small, and slower collisions may be more efficient for deactivation. The mean collision time τ_e was estimated²³ for an interaction length of ~2 Å and the mean velocity at 300 °K, $\overline{v} = (8kT/\Pi\mu)^{1/2}$. For XeCl* (v =100) the vibrational period τ_v is ~4.5×10⁻¹³ sec, and τ_c/τ_v is ~0.3, 0.5, 0.7, 1.0, and 1.1 for He, Ne, Ar, Kr, and Xe, respectively. The match of τ_c and τ_v is best for Kr and Xe which is consistent with larger $\langle \Delta E \rangle$ results in Table III. Of course, the interaction potentials also are more attractive for the heavier rare gases.

In an effort to determine the features of the interaction potential that were important to KBr vibrational deactivation, Matzen and Fisk performed a classical trajectory study for the KBr + Ar system²¹ using three different potentials. Surface I, the best surface, was constructed empirically from the two-body interactions of K^{*}, Br⁻, and Ar and an Ar-KBr interaction term. Surface II was like Surface I but ignored all attractive interactions. Surface III was similar to II but sub-

TABLE III. Summary of energy disposal.

Bath gas gas	Rel	laxation	Transfer		
	$\langle \Delta E_R \rangle^{a}$	λ ^b	$\langle \Delta E_T \rangle^2$	λp	
He	2.1	17.6±0.4	5.0	9,9±0.3	
Ne	3.0 (~15.0) ^c	11.2 ± 0.4 (34.0, 0.5) ^c	6.4	6.6±0.3	
Ar	5.4 (~ 10.0) ^c	4.7±0.4 (16.0, 0.8) ^c	8.3	3.5±0.3	
Kr	9.0	1.5±0.4	12.5	0.4 ± 0.2	

^aMean energy loss in kcal/mole for relaxation $\langle \Delta E_R \rangle = \Sigma P_{ij}^R$ $\Delta E / \Sigma P_{ij}^R$, $\langle \Delta E_T \rangle = \Sigma P_{ij}^T \Delta E / \Sigma P_{ij}^T$.

^bLinear surprisal parameter; the error represents standard deviation to a least-square fit.

^cSecond entry in parenthesis refers to the two components of the vibration relaxation of KBr (from Crim Ref. 21).

stituted a spherically symmetric attractive part for the Ar + KBr interaction. The major differences in the potentials were the attractive interactions. Surface II was purely repulsive while the attractive features of I and II were of the same strength but of different shape. On I the incoming Ar is attracted preferentially to the K⁺ end of KBr while in III the interaction is symmetric.

The results and conclusions of the trajectory study which are pertinent to XeCl* relaxation can be summarized as follows:

(i) Both the shape and strength of the attractive interactions were important. Surface I gave the best agreement with experimental results and the calculated distribution did have a two-component nature.

(ii) The strength of the attractive interaction determined the magnitude of the inelastic cross section and both I and III gave higher calculated cross sections than II.

(iii) The shape of the attractive potential was important in determining the average amount of energy transferred. For KBr + Ar, collisions with the K^{*} end results in larger inelasticities than collisions with the Br⁻ end, and surface I, which attracted the incoming Ar to the K^{*} end of KBr, gave larger inelasticities.

(iv) The high energy component was associated with strong repulsive interactions. Although attractive interactions were important in bringing the collision partners together, large inelasticity was shown only for trajectories which sampled the strongly repulsive regions of the potential energy surface.

The XeCl situation will be more complicated than for KBr-Ar because of multiple surfaces with differing degrees of attractive and repulsive character and because of the coupled vibrational relaxation and electronic state transfer channels.

Although accurate potentials are not known for XeCl*-Rg, qualitative features can be estimated from ab initio²⁴ and diatomic-in-molecules²⁵ calculations which have been reported for some homonuclear trimer systems, Rg_2X (Rg = Ar, Kr and X = F, Cl). The three lowest states of Rg₂X are covalent and repulsive and correlate to RgX(A or X) and Rg; these states are of no importance here. The next three higher states are ionic in nature and bound relative to $Rg_2^* + X^-$. Only the lowest ionic state $(2^{2}B_{2} \text{ in } C_{2v} \text{ geometry})$ though, is bound with respect to $RgX^* + Rg$. The most stable geometry of this lowest ionic state is an isosceles triangle. For the mixed rare gas trimers, such as RgXeCl, the above potentials will be altered somewhat. First, the isosceles triangle geometry will be distorted with the Rg atom drawn closer to the Xe end of XeCl. Secondly, RgXeCl trimers would be expected to be much less strongly bound than Xe₂Cl, paralleling the decreasing binding energy of RgXe* vs Xe₂^{*}. In fact, emission from both Xe₂Cl^{*} and KrXeCl^{*} has been observed.^{26,27} Of the lighter RgXeCl*, only ArXeCl* would be (possibly) weakly bound by more than van der Waals forces. According to the calculations, the bound $\operatorname{Rg}_2^* X^-$ state correlates with $\operatorname{RgX}(C)$ and the next higher ionic $(3^{2}B_{2} \text{ in } C_{2v} \text{ or } 4A' \text{ in } C_{s} \text{ geometry})$ state



FIG. 16. Schematic RgRgX* potentials as a function of α , the Rg-Rg-X bond angle, and the separated Rg+RgX* states to which they correlate. The potential is drawn for a bound trimer, i.e., KrXeCl* or Xe₂Cl*. The $C_{2\nu}$ geometry is realized only for Xe₂Cl*. For the lighter rare gases all the curves become less attractive and finally strictly repulsive in the series Ar < Ne < He.

with $\operatorname{RgX}(B)$. The approach of Rg to $\operatorname{XeCl}(C)$ in C, geometry gives an A' and an A'' state (neglecting spin-orbit interaction) depending on whether the sideways approach of Rg to XeCl is head on or perpendicular to the singly occupied Π orbital. The approach of Rg to XeCl(B) gives only an A' state as shown in Fig. 16. If the C state is higher in energy than the B state, this results in a curve crossing which can lead to collisional coupling of RgX(B), C). Since XeCl(C) is actually lower in energy than XeCl(B), the Rg + XeCl(C) potential should correlate adiabatically to the lowest ionic state of $RgXeCl^*$ (3A' in C_s geometry) as shown in Fig. 16. The Rg + XeCl(B) potential is repulsive and the interaction of the two A'states should be small and collisional mixing of $XeCl^*(B,$ C) should be slow, which is contrary to observation. However, the ab initio calculations show that the collinear approach of Rg to RgX* is also attractive, although the binding is not as large as for the C_s approach, as shown in Fig. 16. In this case approach of Rg to $\operatorname{XeCl}(B)$ is attractive, while $\operatorname{Rg} + \operatorname{XeCl}(C)$ is repulsive. However, the states are of different symmetry, and coupling of XeCl(B, C) via this approach would also be weak unless spin-orbit interaction is included. For such heavy atoms as Kr or Xe this could be of importance and lead to mixing of XeCl(B, C). Even though spin-orbit effects allow mixing of XeCl(B, C), the efficiency of this transfer is still surprising. Furthermore, the rapid B-C transfer holds for all RgX molecules^{3, 4} regardless of the B- and C-state ordering and the magnitude of the spin-orbit interactions. Thus the asymptotic properties of Fig. 16 are not critical for highly vibrationally excited molecules (they may well be of importance for v = 0-5 levels when the transfer rates are 1 or 2 orders of magnitude smaller). Figure 16 also portrays the behavior of the adiabatic potentials as a function of α , the angle between the Rg-Rg-X bonds. As α increases from ~60° to the linear configuration (180°), the 3 A' and 4 A' give rise to an

avoided crossing. This crossing will exist for all RgX^* + Rg and presumably is responsible for electronic state transfer. Apparently the large amplitude motion on the potential curves by highly vibrationally excited RgX^* will lead to frequent sampling of this region where the potentials interact. Furthermore, collisions of both RgX(B) and RgX(C) can sample the lowest potential depending on the approach angle of Rg.

The KBr-Ar trajectory study found that the strength of the attractive interaction determined the magnitude of the inelastic cross sections. This behavior is generally followed here for He-Ar. However, for Kr the relaxation rate constants were much slower with C-B transfer dominating. Only for Kr (and Xe) would the 3 A' potential be significantly bound, and transfer may dominate over relaxation for this reason.

Simple theory would predict that Ar striking the K* end of KBr would result in larger inelasticities than Ar striking the Br^{*} end because K^{*} is much lighter than Br^{*}. In XeCl* the attraction is to the Xe⁺ end rather than the lighter Cl⁻, and our results show somewhat smaller inelasticity for Ar or Ne than in KBr. Because of the stronger attractive interactions and presumably softer repulsions for XeCl*, the present results suggest that the attractive interactions play a more dominant role in XeCl* + Rg than KBr + Rg. Greene et al, ²⁸ in studying the inelastic scattering of CsI by Ar and Xe, suggest that short lived complex may be formed at low collisions energies. Their results fit statistical partitioning of the total energy. Greene et al. also suggest that in the interaction of a highly excited ionic molecule, such as KBr or CsI with Ar, that during the bond extension of the vibration the interaction may resemble Ar interacting with K^{*}. Such an interaction is much stronger than with the molecule leading to stronger attractive interaction during the collision. For XeCl* +Rg this effect will be enhanced because RgXe* is chemically bound (at least for Rg = Kr, Xe) whereas in ArK' the attraction is only electrostatic in nature. We see some evidence for this because of the dependence of the rate constants on vibrational excitation. For the high v the attractive interaction is stronger and leads to larger inelastic cross sections as opposed to the low-v levels where the interaction is more like the weaker Rg-XeCl interaction.

VII. CONCLUSIONS

From computer simulation of the XeCl(B-X) and XeCl(C-A) bound-free emission spectra in He, Ne, Ar, and Kr bath gases, the vibrational and electronic state distributions were assigned for a range of pressures. State-to-state rate constants for vibrational relaxation and electronic state transfer have been assigned for XeCl*(B, C)+Rg collisions by master equation calculations fitting the variation of the vibrational distributions with Rg pressure. The electronic state transfer rate constants for the v = 70-130 range varied from $2.5-15\times10^{-11}$ cm³ molecule⁻¹ sec⁻¹ for the He-Kr series; the vibrational relaxation rate constants are comparable with the exception of Kr which is smaller than for Ar. The magnitude of both the relaxation and transfer rate constants decline by an order of magnitude from v = 100 to $v \cong 10$. The model for state-to-state vibrational relaxation is adequately represented by the exponential gap law. For electronic state transfer the change of vibrational energy is larger than for the collisions giving vibrational relaxation without change in electronic state, and the model is Poisson in nature. The larger loss of vibrational energy associated with electronic statechanging collisions is explained by the attractive potential involved in interconversion of the XeCl(B) and XeCl(C) states.

ACKNOWLEDGMENTS

This work was supported by the Advanced Research Projects Agency of the U.S. Department of Defense (monitored by ONR-N00014-76-0380) and by the U.S. Department of Energy DE-AC02-80ET33068. T.D.D. thanks Phillips Petroleum for a research fellowship. We thank Dr. H. C. Brashears for providing most of the XeCl* spectra for the Xe $({}^{3}P_{1})$ reactions.

- ¹A. Brau, in *Excimer Lasers*, *Topics in Applied Physics*, edited by C. K. Rhodes (Springer, Berlin, 1979), Vol. 30.
- ²(a) W. K. Bischel, H. H. Nakano, D. J. Eckstrom, R. M. Hill, D. L. Huestis, and D. C. Lorents, Appl. Phys. Lett. 34, 565 (1979). (b) R. Burnham, Appl. Phys. Lett. 35, 48 (1979).
- ³(a) L. A. Gundel, D. W. Setser, M. A. A. Clyne, J. A. Coxon, and W. Nip, J. Chem. Phys. 64, 4390 (1976). (b) J. E. Velazco, J. H. Kolts, and D. W. Setser, J. Chem. Phys. 65, 3468 (1976). (c) J. E. Velazco, J. H. Kolts, and D. W. Setser, J. Chem. Phys. 69, 4357 (1978). (d) C. H. Chen, M. C. Payne, C. S. Hurst, and J. P. Judish, J. Chem. Phys. 65, 4028 (1976).
- ⁴(a) J. H. Kolts and D. W. Setser, J. Phys. Chem. 82, 1766 (1978). The XeF data (B/C ratios) presented in this paper are incorrect; for the pressure shown the correct results closely resemble those of XeCl. (b) J. H. Kolts, J. E. Velazco, and D. W. Setser, J. Chem. Phys. 71, 1247 (1979). (c) K. Tamagake, D. W. Setser, and J. H. Kolts, J. Chem. Phys. 74, 4286 (1981).
- ⁵(a) K. Tamagake and D. W. Setser, J. Chem. Phys. 67, 4370 (1977).
 (b) K. Tamagake, J. H. Kolts, and D. W. Setser, J. Chem. Phys. 71, 1264 (1979).
 (c) D. W. Setser, T. D. Dreiling, H. C. Brashears, Jr., and J. H. Kolts, Faraday Discuss. Chem. Soc. 67, 255 (1979).
- ⁶M. F. Golde and A. Kvaran, J. Chem. Phys. **72**, 434, 442 (1980).
- ⁷H. C. Brashears and D. W. Setser, J. Phys. Chem. **84**, 224 (1980).
- ⁸P. J. Marcoux, M. van Swaay, and D. W. Setser, J. Phys. Chem. 83, 3168 (1979).
- ⁹The correct expressions [for the calculations of Ref. 5(b)] for the A-potential and transition moment should read $V(R)^{A,3/2}$ = 1.786×10⁷ exp(-2.8821 R'), $\mu(R) = 70.8 \exp(-1.424 R')$ with R' given in the text. The original expressions in Ref. 5(b) were obtained by neglecting the $(R-R_{d'})^2$ term in the expression for R'.
- ¹⁰(a) P. J. Hay and T. H. Dunning, J. Chem. Phys. 69, 2209 (1978).
 (b) T. H. Dunning and P. J. Hay, J. Chem. Phys. 69, 434 (1978).
- ¹¹M. C. Castex, J. LeCalve, D. Haaks, B. Jordan, and G. Zimmerer, Chem. Phys. Lett. **70**, 106 (1980).
- ¹²(a) E. D. Polaikoft, S. H. Southworth, M. G. White, G. Thornton, R. A. Rosenberg, and D. A. Shirley, J. Chem. Phys. 72, 1786 (1980). (b) G. P. Quigley and W. M. Hughes, Appl. Phys. Lett. 32, 627 (1978).

- ¹³D. W. Setser, H. C. Brashears, and T. D. Dreiling, J. Phys. (Paris) C3, 195 (1980).
- ¹⁴(a) J. Tellinghuisen and M. R. McKeever, Chem. Phys. Lett.
 72, 94 (1980). (b) J. Boker and C. K. Rhodes, J. Chem.
 Phys. 73, 2626 (1980).
- ¹⁵Y. C. Yu and D. W. Setser, J. Chem. Phys. (to be published).

¹⁶W. H. Duewer, J. A. Coxon, and D. W. Setser, J. Chem. Phys. 56, 4355 (1972).

- ¹⁷It is well known that vibrational relaxation follows an experential gap or power scaling low. See, for example, I. Procaccia and R. D. Levine, J. Chem. Phys. **63**, 4261 (1975).
- ¹⁸T. D. Dreiling, Ph.D. thesis, Kansas State University, 1981.
- ¹⁹D. J. Wren, D. W. Setser, and J. K. Ku, J. Chem. Phys. (to be published).
- ²⁰(a) M. S. Chou, F. F. Crim, and G. A. Fisk, Chem. Phys. Lett. 20, 464 (1978). (b) T. Donohue, M. S. Chou, and G. A. Fisk, Chem. Phys. 2, 271 (1973). (c) F. F. Crim, M. S.
- Chou, and G. A. Fisk, Chem. Phys. 2, 283 (1973). (d) F. F.

- Crim. H. B. Bente, and G. A. Fisk, J. Phys. Chem. 78, 2438 (1974).
- ²¹M. K. Matzen and G. A. Fisk, J. Chem. Phys. 66, 1514 (1977).
- ²²F. F. Crim and G. A. Fisk, J. Chem. Phys. **65**, 2480 (1976).
- ²³See, for example, J. I. Steinfeld, J. Chim. Phys. Phys. Chim. Biol. 64, 17 (1967), with application to $I_2(B)^3 \Pi_{0^*u}$, v = 25).
- ²⁴W. R. Wadt and P. J. Hay, J. Chem. Phys. 68, 3850 (1978).
- ²⁵D. C. Huestis and W. E. Schlotter, J. Chem. Phys. 69, 3100 (1978).
- ²⁶F. K. Tittel, W. C. Wilson, R. E. Stickel, G. Marowsky, and W. E. Ernst, Appl. Phys. Lett. **36**, 405 (1980).
- ²⁷H. C. Brashears, D. W. Setser, and Y. C. Yu, J. Chem. Phys. 74, 10 (1981).
- ²⁸E. F. Greene, R. B. Hall, and N. A. Sondergaard, J. Chem. Phys. 66, 3171 (1977).