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TIME RESOLVED STUDY OF RgCl* (B-X) EMISSION AFTER SYNCHROTRON RADIATION

STATE SELECTIVE EXCITATION OF Cl_2^* IN Cl_2/Rg (Xe, Kr, Ar) MIXTURES.

A NEW INSIGHT IN THE B-C ENERGY ORDERING OF RgX STATES

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ABSTRACT

Kinetic results are reported of the decay of the RgCl*(B-X) fluorescence after state selective Synchrotron Radiation excitation of Cl_2^* in Cl_2/Rg (Xe, Kr, Ar) mixtures. A two level collisional mixing model between the B 1/2 and C 3/2 states is compared with the results and allows an estimation of the $\Delta E(B-C)$ energy separation of XeCl and KrCl. ArCl results suggest a more complicated mixing model. For all the three halides our results favours a C state above the B state. The results are discussed and compared with other studies, especially for XeCl, where some controversy exists about ΔE (B-C).

INTRODUCTION

During the last ten years, an increasing amount of experimental and theoretical research about the properties, the formation and decay processes of rare gas halides was stimulated by their laser application. Of specific interest is the energy ordering of the lowest bound excited states, B 1/2 and C 3/2, which are collisionally connected in the decay process of the "laser" B state. A precise evaluation of the energy separation, ΔE (B-C), is difficult in theory and experiment ; XeF, e.g. is a good example of the discrepancy between the respective theoretical (- 400 cm^{-1} ; ref. 1) and experimental (+ $\sim$ 700 cm^{-1}, ref. 2) ΔE (B-C) values. Some controversy exists also about ΔE (B-C) of XeCl (see below). Only a few data exist for KrCl and ArCl.

Two types of experiments yield information about ΔE(B-C). In the first one, the ratio of the steady state intensities of the B-state and C-state emissions, I_B/I_C, is analysed as a function of pressure P or temperature T. It yields the ratio k_{BC}/k_{CB} of the mixing process :
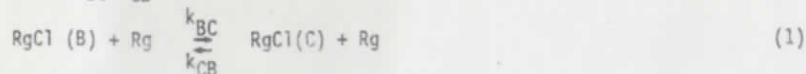
$$RgCl\ (B) + Rg \xrightleftharpoons[k_{CB}]{k_{BC}} RgCl(C) + Rg \qquad (1)$$

Under detailed balance condition, $k_{BC}/k_{CB} = \rho = \exp\ (\Delta E(B-C)/kT)$. In this method, however, some assumptions and approximations are involved, the validity of which must be carefully proved in each particular case. The method was therefore commented recently in detail (ref. 3).

The second approach is based on a direct analysis of the time profiles of the B-state and C-state emissions with their rise and decay rates. The rates are then exploited in a kinetic model describing the formation, mixing, and decay of B- and C-state molecules.

In this paper, the second approach is used to determine $\Delta E(B-C)$ and other relevant kinetic parameters for XeCl, KrCl, and ArCl in Cl_2 doped rare gases. The experiment makes use of the time structure of synchrotron radiation with its nearly δ-like excitation pulses at a high repetition rate. Details of the experiment and of the evaluation of $\Delta E(B-C)$ are given in the next two sections. In the last section, the results are presented and compared with literature results.

EXPERIMENTAL DETAILS

The work was performed at the Hamburger Synchrotron Strahlungslabor HASYLAB at the experimental stations for luminescence spectroscopy described in ref. 4-6. The excitation wavelength λ_{ex} was tuned between the LiF cut-off and $\sim$ 2000 $\overset{\circ}{A}$ at a resolution interval of 1 to 2.5 $\overset{\circ}{A}$. Fluorescence (λ_{an}) was analysed at a resolution interval of 5 to 10 $\overset{\circ}{A}$. Decay curves (λ_{ex} and λ_{an} fixed) were measured with the delayed coincidence technique. The shortest decay time accessible with the fast detectors used (channel plate for λ_{an} < 1800 $\overset{\circ}{A}$; Valvo XP 2020 Q for longer wavelengths) was $\sim$ 100 ps. The gas pressure in the gas cell ranged between 0 and 600 torr (P_{Rg}) and 0-a few torr (P_{Cl_2}). The fluorescence spectra and decay curves were measured for pure Cl_2^* and Cl_2/Rg (Xe, Kr, Ar) mixtures as a function of P_{Cl_2}, P_{Rg}, λ_{ex}, and λ_{an}. Kinetic results related to the decay of RgCl* B → X emission at the "laser wavelength" (bottom of the B well) are presented here as a function of P_{Rg} (P_{Cl_2} fixed at 0.8 torr). With an appropriate λ_{ex}, Cl_2 was initially excited into selected vibronic levels of the $1^1\Sigma_u^+$ or $2^1\Sigma_u^+$ state (ref. 4). This has two advantages : i) Due to the short radiative lifetimes of the primarily excited Cl_2^* states ($\leq$ 3 ns) and the fast quenching by the rare gas, the formation rate is faster than any decay rate of RgCl* involved here. ii) ArCl* can be formed at threshold of the Cl_2^* + Ar reaction (ref. 7).

The decay of RgCl (B → X) emission is attributed to λ^- of the B/C mixing model presented below (λ^- is always the slower one of the two components λ^+, λ^-). The rise of the signal is a superposition of the λ^+ component, the formation rate of the excimer, and the vibrational relaxation of the initially formed

high vibrational levels of the excimer state (XeCl, KrCl). Moreover, it can be superimposed with a fast Cl_2^* fluorescence signal itself (especially in the case of ArCl). A precise analysis of the rise is difficult. The rise times are therefore not exploited here.

DISCUSSION OF THE TWO LEVEL B/C MIXING MODEL

After a δlike excitation at time $t = 0$, the concentration of RgCl molecules in the $v' = 0$ B and C states are supposed to be B_0 and C_0. The time evolution of the concentrations of the molecules interacting via (1) is given by :

$$B(t) = \frac{1}{\lambda^- - \lambda^+} \left[(\ (\lambda^- - \beta)B_0 + \nu C_0)e^{-\lambda^+ t} + ((\epsilon - \lambda^+)B_0 - \nu C_0)e^{-\lambda^- t} \right] \quad (2)$$

$$C(t) = \frac{1}{\lambda^- - \lambda^+} \left[((\ \lambda^- - \gamma)C_0 + \mu B_0)e^{-\lambda^+ t} + ((\gamma - \lambda^+)C_0 - \mu B_0)e^{-\lambda^- t} \right] \quad (3)$$

with the two common exponents :

$$\lambda^\pm = \frac{1}{2}(\beta + \gamma) \pm \frac{1}{2}\left[(\beta - \gamma)^2 + 4 \mu\nu \right]^{1/2} \quad (4)$$

in which :

$$\beta = \frac{1}{\tau_B} + k_{1B}(Cl_2)\ P_{Cl_2} + k_{1B}(Rg)\ P_{Rg} + k_{2B}(Rg)P^2_{Rg} + k_{BC}(Rg)P_{Rg}$$

$$\gamma = \frac{1}{\tau_C} + k_{1C}(Cl_2)\ P_{Cl_2} + k_{1C}(Rg)\ P_{Rg} + k_{2C}(Rg)P^2_{Rg} + k_{CB}(Rg)P_{Rg} \quad \Big\} \quad (5)$$

$$\mu = k_{BC}(Rg)\ P_{Rg} \ ; \qquad \nu = k_{CB}(Rg)P_{Rg}$$

where τ_B and τ_C are the radiative lifetimes ; $k_{1B}(Cl_2)$, $k_{1C}(Cl_2)$, $k_{1B}(Rg)$, $k_{1C}(Rg)$, the two-body quenching rate constants with Cl_2 and Rg ; $k_{2B}(Rg)$ and $k_{2C}(Rg)$ the three-body quenching rate constants by two Rg atoms. Because of our low Cl_2 pressure, B/C mixing by Cl_2 collisions is neglected. In the following we assume that $k_{1B} = k_{1C} = k_1$; $k_{2B} = k_{2C} = k_2$.

Then Eq. (4) is equivalent to :

$$\lambda_\pm = \frac{1}{2}(K_B + K_C) + \frac{1}{2}(k_{BC} + k_{CB})P + k_1 P + k_2 P^2$$

$$\pm \frac{1}{2}\left[(k_{BC} + k_{CB})^2 p^2 + 2 (k_{BC} - k_{CB})(K_B - K_C)P + (K_B - K_C)^2 \right]^{1/2} \quad (6)$$

where $K_B = 1/\tau_B + k_1(Cl_2)P_{Cl_2}$, $K_C = 1/\tau_C + k_1(Cl_2)P_{Cl_2}$ and $P_{Rg} = P$

It is useful to discuss the low and high pressure limit approximations.

1) In the low P case one finds for eq. (6) :

$$\lambda^+ = K_B + k_1 P + k_{BC}P + k_2 P^2 + \frac{1}{4}\ \frac{(k_{BC} + k_{CB})^2 p^2}{(K_B - K_C)} \quad (7)$$

$$\lambda^- = K_C + k_1 P + k_{CB}P + k_2 P^2 - \frac{1}{4}\ \frac{(k_{BC}+k_{CB})^2 p^2}{(K_B - K_C)} \quad (8)$$

In practice and for $P \to 0$, a nearly linear dependence with P is expected for λ^+ and λ^- . The last term is much larger than the $k_2 P^2$ term which can be neglected.

2) In the high P case, eq. (6) is approximated by :

$$\lambda^+ = \frac{K_B k_{BC} + K_C k_{CB}}{k_{BC} + k_{CB}} + (k_{BC} + k_{CB})P + k_1 P + k_2 P^2 \quad (9)$$

$$\lambda^- = \frac{K_B k_{CB} + K_C k_{BC}}{k_{BC} + k_{CB}} + k_1 P + k_2 P^2 \quad (10)$$

λ^+ and λ^- have a parabolic pressure dependence. The λ^- expression is particularly interesting. Note that i) the $(k_{BC} + k_{CB})$ P term of λ^+ is absent in λ^- ; ii) the linear term only contains $k_1 P$; iii) the intercept $\lambda_0^- = \frac{K_B + \rho K_C}{1 + \rho}$ allows a direct estimation of ρ and hence Δ E (B-C) provided that τ_B and τ_C radiative lifetimes are known.

For illustration, Fig. 1 shows the characteristic inflexions of the exact λ^- curves and the critical dependence of λ_0^- on ρ. Three cases (ρ = 1,10,1/10) corresponding to $E_B = E_C$, E_B above E_C by 480 cm^{-1}, E_B below E_C by 480 cm^{-1} are considered. The following parameters which are close to the XeCl case are used : $k_1 = 0.5 \times 10^{-11}$ $cm^3 s^{-1}$; $k_2 = 1.2 \times 10^{-30}$ $cm^6 s^{-1}$ $K_B = 10^8$ s^{-1} ; $K_C = 10^7 s^{-1}$; k_{max} (BC or CB) = 13.5 $\times 10^{-11}$ $cm^3 s^{-1}$

For one case (ρ = 1), λ_0^- is included explicitely.

RESULTS AND DISCUSSION

Fig. 2 shows out experimental decay rates of the RgCl (B-X) emission as a function of P for fixed chlorine pressure of 0.81 torr. The excitation wavelength was λ_{ex} = 1350 Å for XeCl and KrCl which leads to the primary excitation of Cl_2 $1^1\Sigma_u^+$ v' $\sim$ 40 (ref. 4) and 1280 Å for ArCl corresponding to Cl_2 $2^1\Sigma_u^+$ v'=0. The observation wavelength was 3080 Å (XeCl), 2220 Å (KrCl) and 1750 Å (ArCl). Each of the three curves is discussed below in terms of the B/C mixing model.

XeCl

The high pressures results were fitted in accordance with eq. (10). We obtain a λ_0^- intercept of $\sim 6.6 \times 10^7$ s^{-1}. This was reduced by the Cl_2 quenching term to $1/\tau_0 \sim 5 \times 10^7$ s^{-1}. The rate constant $k_1(Cl_2) = 5.8 \times 10^{-10}$ cm^3 s^{-1} was determined separately (ref. 5).
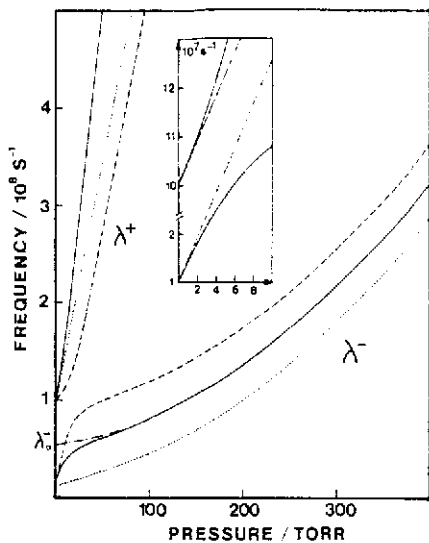
Fig. 1. λ^+ and λ^- curves as a function of P for :
(——) $\rho = 1$;
(...) $\rho = 10$;
(---) $\rho = 10^{-1}$.
The insert shows the low P region for $\rho = 1.\lambda^+$ and λ^- curves are compared with the linear parts of expressions (7) and (8) (see text).
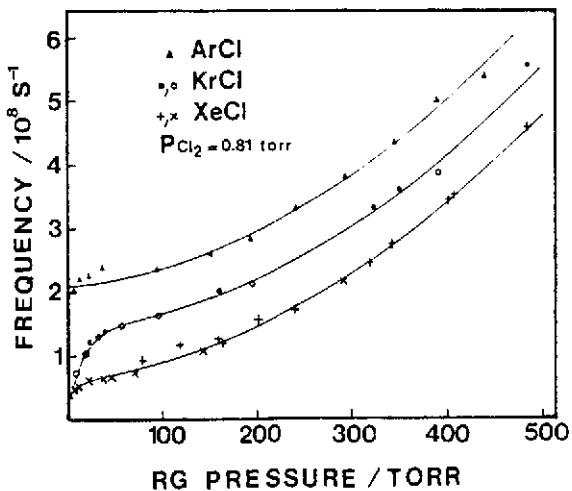

Fig.2. Decay rates of RgCl emissions in Rg/Cl$_2$ mixtures. Values of the different parameters used for the fits are given in the text.

With the experimental radiative lifetimes of XeCl B and C states (11.1 and 131 ns) recently obtained by Inoue et al. (ref. 8) which agree very well with calculations from Hay and Dunning (ref. 1), we see that our $1/\tau_0$ value is very

close to $(1/\tau_B + 1/\tau_C) / 2$ expected when $k_{BC} = k_{CB}$.

Moreover, a good fit of all our experimental results with the complete λ^- expression (4) (fig. 2) is obtained with the following parameters :

k_1 (Xe) $= 0.4 \times 10^{-11}$ cm^3 s^{-1}
k_2 (Xe) $= 1.3 \times 10^{-30}$ cm^6 s^{-1}
k_{BC} $= 13.5 \times 10^{-11}$ cm^3 s^{-1} and $\rho = k_{BC}/k_{CB} = 0.9$.

This would mean that C is above B by 22 cm^{-1}. We thus conclude from our present results that the C state is very near the B state, with a tendency to be above it within the present errors limits.

Comparison with other work

Most of the studies find C below B, and values between + 230 and - 5 cm^{-1} have been published (ref. 3, 8, 9-14). Several determinations have used the high pressure thermal equilibrium intensity ratio I (C-A)/I (B-X). This way of obtaining ΔE(B-C) was recently critically discussed in the case of XeF (ref.3). It must first take into account the B-A fluorescence hidden in the region of the C-A transition (ref. 9). High pressures of the buffer gas are necessary for a complete vibrational relaxation of B and C states but quenching processes either by two or by three-body collisions are generally neglected in the analysis. The effect of neglecting two-body quenching has been underlined in (ref. 3), but three-body quenching effects are still more important at high P as our results clearly show. We thus conclude that steady state intensity ratio results have to be considered with some caution. Studies using the temperature dependence of the intensity ratio (ref. 11, 14) also neglect quenching effects in the analysis, in particular three-body quenching by the rare gas.

Kinetic studies similar to ours in their principle (ref. 15-17) have been reported on XeCl. However these studies do not give evaluation of the ΔE (B-C) energy separation. Probably the observation spectral range was too broad (ref. 15,16), then the kinetics of many vibrational levels are superimposed in the experimental time profile. The pressure conditions may have been either insufficient for considering that the two states are totally collisionnally mixed (ref. 15-17) or too high for neglecting the mixing effect of B and C states (ref. 16). It thus appears to us that most of the effective lifetimes found in the literature for these systems are "λ_0^- intercepts which depend on experimental conditions" and that they can't be simply compared with pure B and C radiative lifetimes.

The recent work of Inoue et al. (ref. 8) is an interesting kinetic study of both B-X and C-A XeCl fluorescences at very low pressure. In particular, it allows a direct and reliable determination of τ_B and τ_C which agree remarkably with theory (ref. 1). The value of $k_{BC}/k_{CB} = 1.5$ (which would correspond to

$\Delta E = + 85$ cm^{-1})given in that paper, is much nearer to our result (C state very near the B state with a tendency to be above it) than e.g. the former results of Setser et al. (ref. 10, 13, 14).

Inoue et al (ref. 8) used the low P approximations (eq. 7 and 8) neglecting the P^2 contribution. Our insert in Fig. 1 indicates that an inclusion of this P^2 contribution would result in a smaller k_{BC}/k_{CB} ratio in even better agreement with our result.

Concerning our $k_1(X_e)$ value, it seems to be more reliable. A good, direct estimate of k_1 is the slope of the λ^- curve in the inflexion region. Using the k_1 value of Inoue et al. (2.3 x 10^{-11} cm^3 s^{-1}), a fit of the measurements in the whole pressure range is not possible. The large value of k may be due to the fact that Inoue et al. neglected B-C mixing by Cl$_2$ itself at partial pressures up to 30 %.

Finally we want to point out that the experimental decay rates themselves measured by Inoue et al., as well as those of Grieneisen et al. (ref. 16) are in good agreement with our present data, if they are reduced to our P_{Cl_2} conditions.

KrCl

Our decay rates of the KrCl (B-X) emission (fig. 2) also compare well with the λ^- expression of the B/C mixing model.

From the intercept of the high P_{Kr} points only (> 80 torr), a value $1/\tau_0 = 1.34$ x 10^8 s^{-1} ($\tau_0 = 7.5$ ns) is obtained after subtraction of the Cl$_2$ quenching term. The rate constant $k(Cl_2) = 4.1$ x 10^{-10} cm^3 s^{-1} was measured before (ref. 18).

For KrCl , τ_B and τ_C have not yet been measured precisely. Only theoretical values are available (ref. 19). From these calculated values (6 and 87 ns) and our experimental intercept, a value $\rho = k_{BC}/k_{CB} = 0.27$ is found giving ΔE (B-C) ~ -275 cm^{-1}.

Good fits of all our present experimental data with the full λ^- expression (4) are obtained (fig. 2) with the following parameters :
$k_1(Kr) = 0.2 \pm 0.1$ x 10^{-11} cm^{3}s^{-1}
$k_2(Kr) = 1.4 \pm 0.1$ x 10^{-30} cm^{6}s^{-1}
$k_{BC} = 2.8 \pm 0.5$ x 10^{-11} cm^{3}s^{-1} and $\rho = 0.16 \pm 0.03$.

This results in a C state above B by $\sim 380 \pm 40$ cm^{-1} which is in fair agreement with the estimate obtained above from the high pressure points. The same energy ordering (C above B) is expected from theory (-660 cm^{-1},ref.19). Good agreement is also found with the experimental ΔE value (-375 cm^{-1},ref.11) deduced from the temperature dependence of the steady state intensity ratio.

Our k_2 (Kr) and $1/\tau_0$ values agree well with Durrett 's results (ref. 20). Concerning the $k_1(Cl_2)$ rate constant, our value is smaller than that used by Durrett in his thesis (6.95 x 10^{-11} cm^3 s^{-1}, ref. 20). However he also measures 2.6 x 10^{-9} cm^{3}s^{-1} for the Cl$_2$ quenching rate constant of the precursor (KrCl B/C mixed state) of Kr$_2$Cl trimer emission in high P_{Kr} experiments. Perharps a mixed three-body quenching term k'_2 (Cl_2,Kr) $P_{Cl_2}.P_{Kr}$ occurs which is not negligible in that case.

Our present k_1(Kr) rate constant is much smaller than the formerly reported value (ref. 18). In our preliminary work, because of less adequate time and spectral resolution conditions, the P^2 loss term was not safely identified and a large mean "two-body rate constant" was obtained from a linear fit of the experimental points between 50 and 500 torr (ref. 18,5). The new value is similar to those presently measured for XeCl and ArCl.

ArCl

Our recent ArCl results are more complicated and they will be published in the near future (ref. 7). We only report here the main features.

The results shown on Fig. 2 are obtained with $\lambda_{ex} = 1280$ Å which corresponds to the excitation energy of the Cl$_2$ $2^1\Sigma_u^+$ (v'=0) state (ref. 4). This excitation wavelength is close to the formation energy threshold of ArCl B state ($\sim$ 1290Å) in the Ar/Cl$_2$ system and allows ArCl to be formed in its lowest vibrational levels. At low pressure, the prompt and fast primary fluorescence of Cl$_2^*$ and probably signal from the low ArCl v' levels show up through the observation band pass of the 1750 Å ArCl B (v' = 0) emission. This difficulty disappears at higher P_{Ar} . The exponential ArCl emission decay of B (v' = 0) has a simple parabolic P dependence (Fig. 2). This is characteristic for a single state decay with linear and quadratic quenching terms.

For higher excitation energies corresponding to Cl$_2 2^1\Sigma_u^+$ (v' > 0), $1/\tau$ curves display a different behaviour with pressure as illustrated by Fig. 3. At low P_{Ar}, in spite of the difficulty mentioned above, due to the Cl$_2^*$ fluorescence, an inflexion is clearly found on the $1/\tau$ curves. At high P_{Ar} (> 200 torr), a very low intensity additional decay component shows up for the highest excitation energies.

The inflexion is observed for all excitation energies above v' = 0 of Cl$_2$ $2^1\Sigma_u^+$: 1265 Å (v' = 1), 1250 (2), 1223 (4) and at 1180 Å (fig. 3). In fig. 8 of another article in this book (ref. 22), an average curve is shown using points obtained with different excitation energies. However, much more points were measured. The various curves given in Fig. 3 connect the results for each particular λ_{ex}. There seems to exist a systematic trend which however should be verified by additional high precision data.

Fig. 3. Comparison of the mean pressure dependences of ArCl B-X decay rates for different excitation wavelengths. The additional low intensity slow decay component for high excitation energies is also indicated (---).
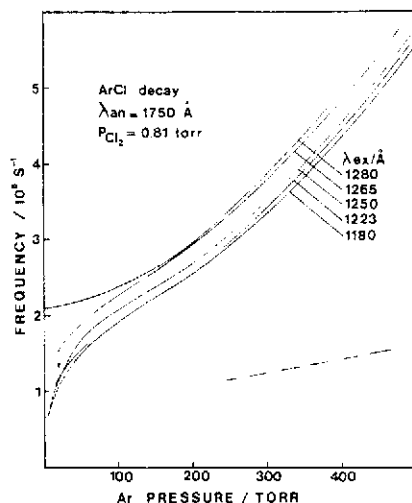
The inflexions were first attributed to the B/C mixing process, indicating a C state much above the B state. For λ_{ex} = 1280 Å the B state alone can be formed and decays without interaction with C.

No theoretical nor experimental data so far exist for ArCl B and C energies or radiative lifetimes. By comparison with ArF and KrCl data, (ref. 19, 21), one expects B and C lifetimes around 4-5 and 50 ns respectively. The radiative lifetime deduced from the "1280" curve, where no B/C mixing appears, is close to the expected B radiative lifetime. For this curve (Fig. 2), a good fit of the data is obtained with :

$$k_1 (Ar) = 0.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$k_2 (Ar) = 1.4 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$$
$$k_{BC} = 0$$

$1/\tau_r$ = 2.1 × 10^8 s^{-1} giving τ_r = 5.2 ns after subtraction of the Cl$_2$ quenching term. $k(Cl_2)$ = 7 ± 0.5 × 10^{-10} cm^{3}s^{-1} was remeasured separately (ref. 7). For the same reasons as in the case of KrCl, the present results are more reliable than those previously reported (ref. 18).

From fig. 3, an estimation of the C threshold energy (∼ 1260 Å) seems possible which would result in a ΔE (B-C) separation of - 1800 ± 500 cm^{-1} , a very high value with regard to the two level B/C mixing model concept. The corresponding ρ value would be of the order of 10^{-4} and we would expect a strong angular type shape of the λ^- curve, which is not observed experimentally. Furthermore, we want to point out that the decay of the time profiles shows slight deviations

from an exponential behaviour. This is observed in particular in the low pressure region and also indicates a rather complicated kinetic scheme. Thus, the physical system can no more be approximated by the simple two level model but rather by a two ladder vibronic one.

Such a model was recently tested (ref. 23) and a good agreement could be obtained qualitatively with the experimental observations. The model calculations show the critical effect of the respective values of the $C_{v'=0} \to B_{v'}$ transfer and $B_{v'} \to B_{v'=0}$ vibrational relaxation rate constants.

For high P_{Ar}, an approximate superposition of the different curves (fig.3) with that of the non interacting B state is obtained when both $C_{v'=0} \to B_{v'}$ transfer and $B_{v'} \to B_{v'=0}$ relaxation are fast processes compared to the $B_{v'=0}$ decay rate. Curves slightly below could be fitted with lower value of the vibrational relaxation rate constant. As expected, calculations show that the decay rate changes with time and that the experimental "exponential decay constants" are only average approximations.

However, this model does not account for the slow additional decay component observed for high P and high excitation energies (fig. 3). It seems worthwhile to notice that in the ArCl system, the D 1/2 state is situated at 1800 cm^{-1} above B 1/2 (ref. 24-26). The C state would thus be very near the D state and it might be necessary to take into account a B/C/D mixing process. As a matter of fact recent results on ArCl (ref. 26) and other rare gas halides suggest the occurrence of collisional transfer from D 1/2 to B 1/2 state.

REFERENCES

1 P.J. Hay and T.H. Dunning, J. Chem. Phys., 69 (1978), 2209-2220
2 H. Helm, D.L. Huestis, M.J. Dyer and D.C. Lorents, J. Chem. Phys., 79 (1983) 3220-3226
3 A. Gedanken and A.L. Smith, J. Phys. Chem. 85 (1981), 2820-2826
4 T. Möller, B. Jordan, P. Gürtler, G. Zimmerer, D. Haaks, J. Le Calvé and M.C. Castex, Chem. Phys., 76 (1983) 295-306
5 B. Jordan, Thesis, University of Hamburg, 1983
6 P. Gürtler, E. Roick, G. Zimmerer and M. Pouey, Nucl. Inst. and Methods, 208 (1983) 835-839
7 T. Möller, B. Jordan, G. Zimmerer, D. Haaks, J. Le Calvé and M.C. Castex, to be published
8 G. Inoue, J.K. Ku and D.W. Setser, J. Chem. Phys. , 80 (1984), 6006-6019
9 P.S. Julienne and M. Krauss, Appl. Phys. Lett. 35 (1979) 55-57
10 H.C. Brashears and D.W. Setser, J. Phys. Chem. , 84 (1980) 224-226
11 J. Tellinghuisen and R.Mc Keever, Chem. Phys. Lett. 72 (1980) 94-99
12 J. Bokor and C.K. Rhodes, J. Chem. Phys. 73 (1980) 2626-2628
13 T.D. Dreiling and D.W. Setser, J. Chem. Phys. 75 (1981) 4360-4378
14 Y.C. Yu, D.W. Setser and H. Horiguchi, J. Phys. Chem. 87 (1983) 2199-2209
15 K.Y. Tang and D.C. Lorents, in Proc. Int. Conf. on Lasers, New Orleans, 1980; STS Press, Mc Lean VA, USA, 1981, 692-698
16 H.P. Grieneisen, Hu Xoe-Jing and K.L. Kompa, Chem. Phys. Lett. 82 (1981) 421-426

17 L.A. Levin and R.E. Center, Report to DOE, Mathematical Sciences Northwest, 1982

18 M.C. Castex, J. Le Calvé, D. Haaks, B. Jordan and G. Zimmerer, Chem. Phys. Lett. 70 (1980) 106-111

19 N.W. Winter, Lawrence Livermore Lab. report, 1977, private communication

20 M.S. Durrett, Thesis, Rice University, Houston, 1982

21 T.H. Dunning and P.J. Hay, J. Chem. Phys. 69 (1978) 134-149

22 G. Zimmerer, lecture 62, this volume

23 D. Haaks, private communication

24 L.A. Gundel, D.W. Setser, M.A.A. Clyne, J.A. Coxon and W. Nip, J. Chem. Phys. 64 (1976) 4390-4410

25 M.F. Golde and R.A. Poletti, Chem. Phys. Lett. 80 (1981) 23-28

26 J. Liegel, Thesis, University of Würzburg (R.F.A.) 1984.