MECHANISM OF COLLISION-INDUCED INTERSYSTEM CROSSING IN CO

D. GRIMBERT, M. LAVOLLÉE, A. NITZAN [*] and A. TRAMER

Laboratoire de Photophysique Moléculaire C.N.R.S. and LURE, Université Paris-Sud, 91405-Orsay, France

We have studied inert-gas pressure effects on the fluorescence decay in CO selectively excited to the $v = 0$ to 7 vibronic levels of the A $^1\Pi$ electronic state. It is shown that the dependence of the quenching cross section σ_{isc} on the average value of the S–T mixing coefficient $\langle \beta^2 \rangle$ has a quasi-logarithmic form. A simple two-level model describing semiquantitatively this behavior is proposed.

1. Introduction

The fluorescence quenching and phosphorescence induction by collisions with inert partners (e.g. rare gases) is a common feature of small (CO [1,2], glyoxal [3]) and intermediate (pyrazine [4], biacetyl [5], etc.) molecules. As shown first by Gelbart and Freed [6,7], these processes may be described in terms of collision induced transitions between "mixed" molecular states:

$$|n\rangle = \sum_s \alpha_{ns} |S\rangle + \sum_t |T\rangle \, ,$$

$$\alpha_n^2 = \sum_s \alpha_{ns}^2 \, ; \quad \beta_n^2 = \sum_t \beta_{nt}^2 \, , \tag{1}$$

where S and T are pure spin states. In the following we denote mixed states as $\hat{S}$ (for $\alpha^2 > \beta^2$) anf $\hat{T}$ (for $\beta^2 > \alpha^2$).

In small molecules, cross sections for the collision-induced intersystem crossing (CI ISC), σ_{isc}, show a pronounced dependence on the properties of the collider [3,8] and may be correlated to its polarizability [8] or to the energy-well depth of the collisional complex [9]. This suggests the important role of the attractive part of the intermolecular potential for CI ISC, as it is the case for rotational relaxation.

A unified treatment of CI ISC and of the rotational relaxation was given by Freed [7]. A principal conclusion of this work is a linear dependence:

$$\sigma_{isc} = \beta^2 \sigma_R \tag{2}$$

(where σ_R denotes an averaged rovibronic relaxation cross section involving a single electronic manifold). This relation deduced from the first-order perturbation treatment (i.e. strictly valid in the weak-coupling limit) has never been experimentally checked.

In this work, we have studied the effect of collisions with rare gases (X = He, Ar, Kr) on the CO fluorescence decay under a selecitve excitation of single vibronic levels ($v' = 0$ to 7) of the A $^1\Pi$ state, coupled to quasi-resonant levels of a' $^3\Sigma^+$, e $^3\Sigma^-$ and d $^3\Delta$ triplet states. Coupling constants being known from high-resolution spectroscopic studies [10], the mixing coefficients of individual rovibronic levels, α_n and β_n, have been evaluated and checked by a study of the collision-free fluorescence decay [11]. Under the present experimental conditions the S–T transition involves many initial levels: if the rotational relaxation within a singlet vibronic state is fast as compared to CI ISC, the initial state is a mixture of rotational levels with Boltzmann populations:

$$N(J) = (2J' + 1) \exp[-\hbar c B'J'(J' + 1)/kT] \, . \tag{3a}$$

On the other hand if rotational relaxation is slow, the populations $N(J)$ are determined by the initial excita-

tion process:

$$N(J) = \sum_{\phi=P,Q,R} \alpha^2(J')S_\phi(J')$$

$$\times \exp[-\hbar c B'' J''(J'' + 1)/kT] \,, \qquad (3b)$$

where $S_\phi(J')$ is the rotational line strength [12]. In either case the mixed character of a given vibronic level is roughly determined by the average:

$$\langle \beta^2 \rangle = \sum_J \beta^2(J)N(J) / \sum_J N(J) \,. \qquad (4)$$

The $\langle \beta^2 \rangle$ values obtained from eq. (4) using eqs. (3a) or (3b) are listed in table 1. It is seen that both calculations yield about the same results.

Complete results of this work will be published elsewhere, this paper contains only preliminary data concerning σ_{isc} for a few collision partners and a preliminary model treatment.

2. Experimental and results

The CO fluorescence was excited by synchrotron radiation of the Orsay Collision Ring (ACO) using a specially designed monochromator [13] with spectral slits of the order of 10–15 Å ensuring a good separation of individual vibronic bands and a constant intensity distribution within a contour of a single band.

The CO pressure was maintained constant (5–20 mtorr) and that of added gases was varied between 0 and 200 torr. Correlated single-photon counting technique adapted to specific properties of the light source [14] was used for recording the fluorescence decay curves.

In collision-free conditions, the CO fluorescence decays quasi-exponentially with lifetimes varying with v in the 9–12 ns range [11]. In the presence of a collider the decay becomes strongly non-exponential and may be approximated by a bi-exponential function (fig. 1). It has been shown [15,16] that the long component of the decay is due to the reversible character of CI ISC and to the vibrational relaxation processes, while the short one practically unaffected by vibrational relaxation, characterizes the initially excited vibronic level and obeys the Stern–Volmer relation:

$$1/\tau(p_X) = 1/\tau(0) + k_{st} p_X \,,$$

where $k_{st} = \sigma_{isc}\langle v \rangle$ is the rate constant of the S–T CI ISC. σ_{isc}, for different vibronic states and different collision partners, is given in table 1.

It may be clearly seen that there is no regular variation of σ_{isc} with v' but a net correlation between σ_{isc} and $\langle \beta^2 \rangle$. We do not observe, however, the linear correlation expected from the first-order perturbation treatment [cf. eq. (2)]. If we suppose that no transitions between pure singlets and pure triplets can oc-

Table 1

Mixing coefficients $\langle \beta^2 \rangle$ and quenching cross section σ_{isc} for vibronic levels of the A$^1\Pi$ state. Relative error in σ_{isc} values is ± 10%

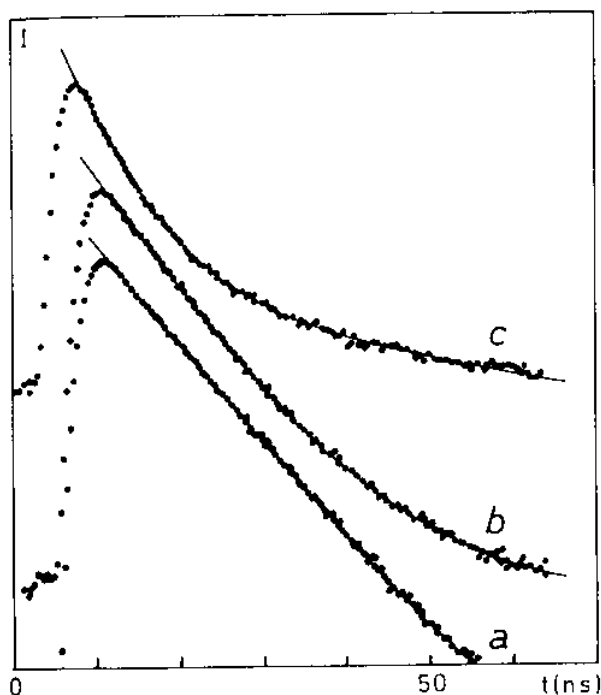| V	Perturbing levels	$\langle \beta^2 \rangle$ from		σ_{isc} (A^2)		
		eq. (3b)	eq. (3a)	He, A = 45 cm^{-1}, $1/a$ = 3.13 A	Ar, A = 150 cm^{-1}, $1/a$ = 3.56 A	Kr, A = 185 cm^{-1}, $1/a$ = 3.65 A
0	e$^3\Sigma^-$ (v = 1) d$^3\Delta$ (v = 4)	0.102	0.092	3.4	27	44
1	d$^3\Delta$ (v = 5) a'$^3\Sigma^+$ (v = 10)	0.062	0.080	2.7	25	43
2	e$^3\Sigma^-$ (v = 4)	0.0044	0.0032	0.9	10.1	32
3	d$^3\Delta$ (v = 8)	0.003	0.003	0.45	9.1	29.5
4	a'$^3\Sigma^+$ (v = 14)	0.012	0.016	1.35	17.5	45.5
5	e$^3\Sigma^-$ (v = 8)	0.002	0.0019	0.55	12.4	30.5
6	d$^3\Delta$ (v = 12) a'$^3\Sigma^+$ (v = 17)	0.102	0.084	3.6	23.2	44.5
7	e$^3\Sigma^-$ (v = 11)	0.001	0.0012	0.5	9.8	36

Fig. 1. Experimental decay curves (corrected for the black-counting and stray-light background) for $v' = 2$ level of CO. $p_{CO} = 12$ mtorr. (a) $p_{Ar} = 0$, (b) $p_{Ar} = 4$ torr, (c) $p_{Ar} = 35$ torr.

cur i.e. that $\sigma_{isc} \to 0$ for $\beta^2 \to 0$ and if we neglect the possibility of heavy-atom effects, the variation of σ_{isc} with $\langle \beta^2 \rangle$ may be described in the following way:
(i) Initially, σ_{isc} increases rapidly and quasi-linearly wiht $\langle \beta^2 \rangle$; for higher $\langle \beta^2 \rangle$ it attains a limiting value σ_{max} dependent on the collision partner.
(ii) This "saturation" takes place more rapidly for heavy (large mass, large polarizability) perturbers.

3. Model calculation

The experimental data demonstrate that the linear dependence predicted by the first-order perturbation treatment breaks down for the observed range of coupling strengths. It is natural to associate this observation with the breakdown of the linear approximation. In order to test this viewpoint, we checked whether the observed phenomena may be fitted to calculations based on a non-perturbative solution of extremely simplified two-level models with physically reasonable parameters. The collision is treated semi-classically so that the coordinate of the perturbing atom is taken as a time-dependent classical function in the interaction hamiltonian. For simplicity the interaction is assumed to depend only on the separation between

the centers of mass of the colliding particles. Following Freed [7] we also assume that this interaction which induces the coupling between $|SJ\rangle$ and $|TJ'\rangle$ levels is proportional to the mixing coefficient β [eq. (1)] and to the collisional coupling between rotational levels of the S (or T) state:

$$V_{\hat{S}J,\hat{T}J'} = \beta V_{SJ,SJ'} .$$

Note that this collisional coupling does not conserve the molecular angular momentum so that levels characterized by different rotational quantum numbers J may be collisionally coupled.

With the objective of obtaining rough estimates we make some more drastic assumptions:

(1) Level shifts are disregarded.

(2) Two simple choices of interaction potentials are made:

(a) A square perturbation, different from zero during a collision time τ_c

$$\tau_c = 1/av \tag{5}$$

and given during this time by

$$V = \pi^{1/2} \beta A e^{-a^2 b^2} , \tag{6}$$

where b is the impact parameter, a measures the range of the interaction potential and A its strength. v is the relative velocity of the colliding particles. Eqs. (5) and (6) are obtained by fitting a gaussian interaction

$$V_{\hat{S}\hat{T}}(t) = \beta A e^{-a^2 R^2(t)} = \beta A e^{-a^2 b^2 - a^2 v^2 t^2} \tag{7}$$

to a square potential taking

$$\tau_c = \left[\int_{-\infty}^{\infty} dt\, t^2 V(R(t)) / \int_{-\infty}^{\infty} dt\, V(R(t)) \right]^{1/2} \tag{8}$$

and

$$V = (1/\tau_c) \int_{-\infty}^{\infty} V(R(t))\, dt . \tag{9}$$

(b) A time-dependent perturbation of the form

$$V_{ST}(t) = C_1 \, \text{sech}(C_2 t) , \tag{10}$$

where C_1 and C_2 were determined so that τ_c and V defined by eqs. (8) and (9) are again given by eqs. (5) and (6). This leads to

$$C_1 = \tfrac{1}{2}\pi^{1/2}\beta A e^{-a^2 b^2} , \tag{11}$$

$$C_2 = \tfrac{1}{2}\pi av . \tag{12}$$

The transition probability in a collision with a given impact parameter, b, is obtained by solving the time-dependent Schrödinger equation. This gives in case (a):

$$P(b, v) = \frac{\pi \bar{A} \beta^2 e^{-2a^2 b^2}}{2(1 + \pi \bar{A}^2 \beta^2 e^{-2a^2 b^2})}$$

$$\times \left[1 - \cos \frac{(1 + \pi \bar{A}^2 \beta^2 e^{-2a^2 b^2})^{1/2}}{\bar{v}} \right] , \tag{13a}$$

where $\bar{A} = 2A/\delta E$ and $\bar{v} = 2\hbar a v/\delta E$ and in case (b) (according to ref. [17]):

$$P(b, v) = \sin^2(\pi^{1/2} \bar{A} \beta e^{-a^2 b^2}/\bar{v}) \operatorname{sech}^2(2/\bar{v}) . \tag{13b}$$

The total cross section for a given velocity v:

$$\sigma_{isc}(v) = 2\pi \int_0^\infty P(b, v) b \, db$$

will be, for case (a):

$$\sigma_{isc}(v) = (\pi/4a^2)\{\ln(1 + \pi \bar{A}^2 \beta^2) + 2C_i(1/\bar{v})$$

$$- 2C_i[(1 + \pi \bar{A}^2 \beta^2)^{1/2}/\bar{v}]\} \tag{14a}$$

and for case (b):

$$\sigma_{isc}(v) = (\pi/2a^2) \operatorname{sech}^2(2/\bar{v})$$

$$[\gamma + \ln(2\pi^{1/2} \bar{A} \beta/\bar{v}) - C_i(2\pi^{1/2} \bar{A} \beta/\bar{v})] , \tag{14b}$$

where γ is the Euler constant. This result may be numerically averaged for Maxwell—Boltzmann distributions corresponding to different colliding pairs and temperatures in order to evaluate the effective cross section defined as:

$$\sigma_{isc} = \langle \sigma_{isc}(v) v \rangle / \langle v \rangle .$$

These formulae are applied to the CO case with the following choice of parameters: $\delta E = 10 \text{ cm}^{-1}$ (of the order of the average gap between the closest lying $\tilde{S}$ and $\tilde{T}$ states for $v' = 0$, 1 and 2 A$^1\Pi$ CO levels); $A_{CO,He}$ is taken from ref. [18] while for other gases we suppose $A_{CO,X}/A_{CO,He} = (\epsilon_X/\epsilon_{He})^{1/2}$ where ϵ is the Lennard-Jones constant; $1/a$ is equal to the averaged Lennard-Jones radius $(\sigma_{CO} + \sigma_X)/2$. σ and ϵ parameters are taken from ref. [19].

Plots of σ_{isc} versus $\ln(\beta^2)$ obtained in this way for cases (a) and (b) are compared with experimental data in fig. 2.
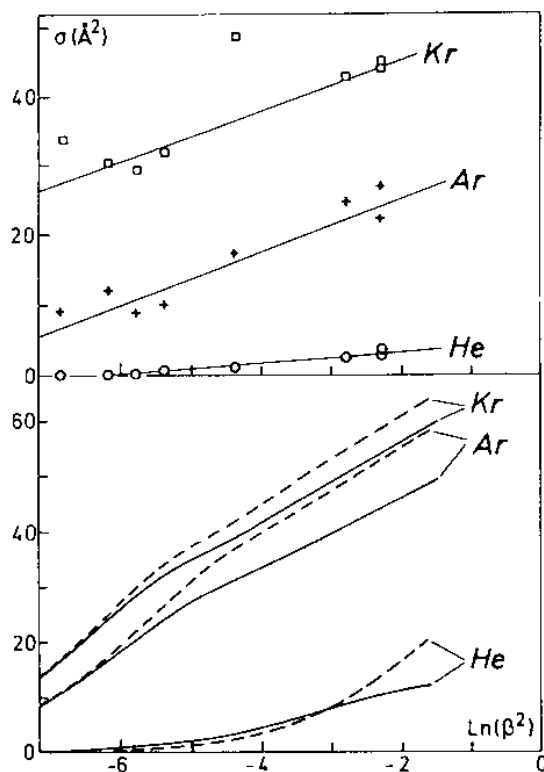

Fig. 2. σ_{isc} plotted versus $\ln\langle\beta^2\rangle$. Top: experimental values. Bottom: calculated values for case (a), dotted line, and case (b), solid line, for different collision partners.

4. Comments

(1) It has been shown that with a reasonable choice of parameters we obtain a correct order of magnitude for σ_{isc} and reproduce fundamental features of the observed behavior (saturation, dependence on the collision partner.

(2) In the weak perturbation limit ($A\beta \to 0$), eqs. (14a) and (14b) give a linear dependence of σ_{isc} on β^2, deduced previously from the first-order perturbation treatment [7].

(3) The two model potentials [eqs. (5) and (6) for case (a), eq. (10) for case (b)] were chosen because they lead to analytically soluble problems. The close similarity between the results obtained in both cases suggests that at least in the range of parameters considered, the exact form of the perturbation is relatively unimportant. This is seen in the range $\bar{v} \gg 1$ where

$$\sigma = (\pi/2a^2)\bar{A}^2\beta^2/4\bar{v}^2 \text{ for case (a) and}$$

$$\sigma = (\pi/2a^2)\bar{A}^2\beta^2/\bar{v}^2 \text{ for case (b).}$$

For $\bar{v} \lesssim 1$ the results of the two models disagree

with each other because the square potential cannot account correctly for the adiabatic behavior in this limit.

(4) Our model neglecting the level shifts is complementary to that of Freed and Tric [20] accounting for level shifts by the first-order perturbation treatment and for the level crossing in the spirit of the Landau—Zener approach.

Acknowledgement

References

[1] T.G. Slanger and G. Black, J. Chem. Phys. 58 (1973) 194, 3121.

[2] E.H. Fink and F.J. Comes, Chem. Phys. Letters 14 (1972) 433.

[3] R.A. Beyer and W.C. Lineberger, J. Chem. Phys. 62 (1975) 4029.

[4] A. Frad, F. Lahmani, A. Tramer and C. Tric. J. Chem. Phys. 60 (1974) 4419.

[5] R. van der Werff and J. Kommandeur, Chem. Phys. 16 (1976) 125.

[6] W.M. Gelbart and K.F. Freed, Chem. Phys. Letters 18 (1973) 470.

[7] K.F. Freed, J. Chem. Phys. 64 (1976) 1604.

[8] C.A. Thayer and J.T. Yardley, J. Chem. Phys. 61 (1974) 2487.

[9] C.S. Parmenter, Discussion at the Meeting on Radiationless Processes, Breukelen (1977).

[10] R.W. Field, B.G. Wick, J.D. Simmons and S.G. Tilford, J. Mol. Spectry. 44 (1972) 383.

[11] R.W. Field, M. Lavollée, R. Lopez-Delgado and A. Tramer, to be published.

[12] G. Herzberg, Molecular spectra and molecular structure, Vol. 1 (Van Nostrand, Princeton, 1962).

[13] M. Lavollée and R. Lopez-Delgado, Rev. Sci. Instr. 48 (1977) 816.

[14] R. Lopez-Delgado, A. Tramer and J. Munro, Chem. Phys. 5 (1974) 72.

[15] M. Lavollée and A. Tramer, Chem. Phys. Letters 47 (1977) 523.

[16] M. Lavollée and A. Tramer, to be published.

[17] N. Rosen and C. Zener, Phys. Rev. 40 (1932) 502.

[18] S. Green and P. Thaddeus, Astrophys. J. 205 (1976) 766.

[19] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular theory of gases and liquids (Wiley, New York, 1954).

[20] K.F. Freed and C. Tric, Chem. Phys., to be published.