

# CHANGE IN TOTAL ANGULAR MOMENTUM WITHIN THE $z^3F^0$ TITANIUM EXCITED STATE INDUCED BY COLLISIONS WITH HYDROGEN AND NITROGEN MOLECULES

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Collisions that produce a change in the total angular-momentum and quenching processes involving the triplet  $z^3F^0$  titanium excited level and diatomic molecules have been studied by laser perturbation and time-resolved spectroscopy. The thermally averaged total angular-momentum changing cross sections ( $z^3F_i^0 \rightarrow z^3F_j^0$ ) in units of  $10^{-16} \text{ cm}^2$  are:  $\bar{\sigma}_{42} = 3.2 \pm 1, 1.4 \pm 0.5$ ;  $\bar{\sigma}_{43} = 13.3 \pm 2, 6.8 \pm 1$ ;  $\bar{\sigma}_{32} = 19.0 \pm 2, 7.2 \pm 1$ , respectively, for nitrogen and hydrogen colliding partners.

Large quenching cross sections are obtained, as  $\bar{\sigma}_O^{N_2} = 53 \pm 7$ , and  $\bar{\sigma}_O^{H_2} = 38 \pm 4$  in units of  $10^{-16} \text{ cm}^2$ .

These results are discussed in relation with previous measurements dealing with titanium—noble-gas collisions, and with available published results.

KEY WORDS: atom-molecule collision cross sections, quenching, titanium

## I. INTRODUCTION

In a previous paper,<sup>1</sup> we have reported laser-induced perturbation measurements of quenching and total angular-momentum changing cross sections within the  $z^3F^0[3d^2(^3F) - 4s4p(^3P^0)]$  excited state of titanium atom, induced by collisions with argon, neon, and helium noble-gases. In the present paper, these measurements are extended to collisions with hydrogen and nitrogen molecules.

As for collisions with noble-gas atoms, excitation transfer processes and quenching mechanisms involving transition metal atoms in excited states and molecules, remain poorly studied. Indeed, though experiments have been done mainly on atoms of group II.B (Cd,<sup>2,4,5</sup> Zn,<sup>6-8</sup>) and group II.A (Mg,<sup>10,11</sup> Ca<sup>9</sup>), and

theoretical works have been achieved on reactive collisions for systems such as Cu-H<sub>2</sub><sup>15</sup> and Mg-H<sub>2</sub>,<sup>12</sup> to our knowledge no data have been published on "refractory" metal atoms, despite their interest as well from a fundamental point of view, as for their potential use for applications in physics and chemical physics.

On the contrary, these elementary processes have been extensively studied for alkali-metal atoms, for Li,<sup>16-19</sup> Na,<sup>20-23</sup> K,<sup>24-28</sup> Rb,<sup>29-32</sup> Cs<sup>33-35</sup> and large differences have been observed between the measured cross sections for quenching and excitation transfers induced by collisions with molecules, and the corresponding results obtained for collisions with noble-gases.

These differences have stimulated numerous theoretical works and substantial progress in understanding the involved basic mechanisms, has been made during recent years. Indeed, if there is a near-resonance between the fine-structure energy splitting of alkali-metal atom excited state and a rotational transition of the molecule, an enhanced cross section may be expected.<sup>36,45-47</sup> Moreover, when the collision partner is a molecule instead of a rare-gas, an additional region of non-adiabatic coupling caused by the anisotropy of the molecule, may largely influence fine-structure transitions of alkali-metal atom induced by collision<sup>37-38</sup> and the passage through an intermediate ionic complex  $A^+X_2^-$  (A is the alkali-metal atom and X<sub>2</sub> the diatomic molecule), has been assumed to cause mixing of the alkali-metal atom fine-structure levels.<sup>39</sup> This "ionic intermediate" model has been also used in the earlier theoretical approaches of quenching phenomena,<sup>40</sup> and served as a useful guideline for further studies.

At the present time, potential energy surfaces for some prototype systems like Li-H<sub>2</sub>,<sup>41</sup> Na-H<sub>2</sub><sup>42</sup> and Na-N<sub>2</sub><sup>43</sup> are available, pseudo-potential molecular-structure calculations for all alkali-metal atom-H<sub>2</sub> system have been achieved<sup>44</sup> and recently quantum-mechanical calculations of fine structure transition cross-sections for Rb(5<sup>2</sup>P<sub>J</sub>) + H<sub>2</sub>, D<sub>2</sub> collisions have pointed out the primary importance of perturber rotational levels and bring clarification on the near resonance phenomena.<sup>45,46,47</sup>

Collisions between an alkali-metal atom in excited state and a molecule may also give rise to reactive processes, for example a recent theoretical study of the reaction Cs(7p) + H<sub>2</sub> → CsH + H has been developed, pointing out the strong influence of ionic intermediate.<sup>48</sup>

These works allow at least, a semi-quantitative understanding of quenching and excitation transfer mechanisms involving alkali-metal atoms in excited states and diatomic molecules.

Since in our previous work,<sup>1</sup> we have found similarities between total angular-momentum changing cross sections within the  $z^3F^0$  excited state of titanium induced by collisions with noble-gases, and corresponding processes for alkali-metal atoms, it was interesting to extend our measurements to hydrogen and nitrogen molecular colliding partners.

Quenching mechanisms and total angular-momentum changing processes involving the  $z^3F_j^0[3d^2(^3F)4s4p(^3P^0)]$  sublevels of titanium atoms in collisions with hydrogen and nitrogen molecules, are studied using the same experimental device as in Ref. 1. Titanium atoms are produced by sputtering in a hollow-cathode discharge, and they are injected in a pressure-controlled observation chamber. Then quenching

mechanisms and fine-structure changing collisions are studied by selective laser excitation and time-resolved spectroscopy. Reaction rates are deduced from fluorescence light intensity relaxation curves using a numerical identification method derived from the method previously used for helium.<sup>49,50</sup>

## II. EXPERIMENT

The experimental device was described in details in Ref. 1. Let us just recall the essential features of the experiments. The titanium atoms are produced by sputtering in a hollow-cathode discharge, and they are injected together with the buffer-gas atoms (argon or neon) into the observation chamber, leading to an after glow expanding jet. The observation chamber is equipped with fused silica windows, allowing spectroscopic investigations along two perpendicular axes at right angles to the expanding jet. Hydrogen or nitrogen gases are injected directly into the observation chamber, and a constant gas flow is obtained by means of a 35 m<sup>3</sup>/h pump (Alcatel) and mass-flow-rate controllers (Tylan). Pressure value in the observation chamber is measured by an absolute capacitance manometer (MKS Baratron). Satisfactory titanium sputtering conditions are obtained for buffer-gas flow rates (argon or neon in the range 200 to 1000 cm<sup>3</sup> min<sup>-1</sup> (STP) discharge current intensities  $I_d$  higher than 15 mA, and rise a maximum for pressure values (measured in the observation chamber) of 0.8 mb and 1.3 mb, respectively for argon and neon buffer gases. In these conditions typical concentrations of about  $3 \times 10^{10}$  cm<sup>-3</sup> titanium atoms in ground state ( $a^3F_2$ ) are obtained in the region of laser perturbation studies, situated 15 cm downstream from the hollow-cathode exit hole. As in Ref. 1, the gas temperature  $T$  is deduced from measurements of population densities on the  $j = 2, 3$  and 4 sublevels of the  $a^3F$  titanium ground state, assuming a Boltzmann population distribution. In all cases under study, we found  $T = 400 \text{ K} \pm 25 \text{ K}$ .

In all the experiments, high-purity-grade gases are used (Air Liquide 99.9995%), and the hollow-cathode consists of 99.9% pure polycrystalline titanium. Between each experiment, the whole device is maintained down to a pressure of  $10^{-7}$  mb by secondary pumping.

In the region of laser perturbation studies, 15 cm down stream from the cathode exit hole, the light emission from the expanding jet is very weak, and the species inside the medium are mainly the buffer gas (argon or neon) in ground state, the auxiliary gas (nitrogen or hydrogen molecules) in ground state, and titanium atoms in ground ( $a^3F$ ) and metastable ( $a^5F$ ) states, as shown in Ref. 1.

A nitrogen-laser-pumped tunable dye laser (spectral width 0.4 Å, pulse width 1 ns, energy per pulse 2 μJ, repetition rate 20 Hz; EG and G, Princeton Applied Research PAR 2100 Dyescan) is used to selectively populate a fine-structure sublevel of the  $z^3F^0$  titanium state from the  $a^3F$  ground state. The laser-induced fluorescence light emission, observed at right angles to both the laser beam and the jet axis, is imaged by a fused silica lens ( $f = 200$  mm), with a magnification of unity, onto the entrance slit of a 100 cm grating spectrometer (THR 1000, Jobin-Yvon, resolving power  $\sim 100\,000$ ), equipped with a RCA 7265 photomultiplier tube (rise time, 2 ns).

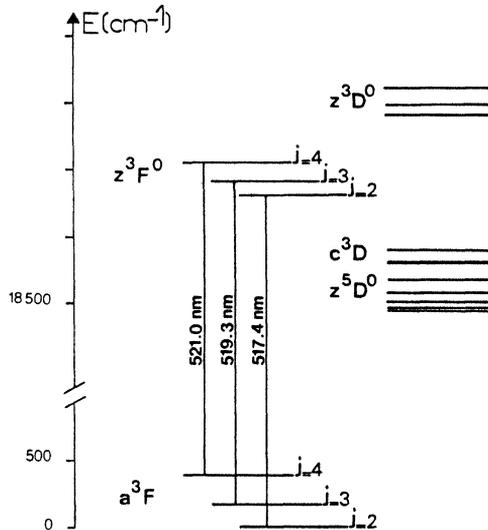
Then the time dependence of the output signal is analysed, in this experiment, by a 400 MHz Tektronics 7912 AD programmable digitizer synchronized with the laser pulse and connected to a desktop computer. As in Ref. 1, great care is taken to prevent saturation of the electronic devices by fluorescence light and stray laser light. The laser beam is collimated and attenuated by neutral-density filters, in order to reduce the interaction volume and also to eliminate laser- and population-induced phenomena such as superradiance or superfluorescence. Finally, each relaxation curve corresponds to an average of at least 256 laser shots.

### III. MEASUREMENTS

The simplified diagram of the titanium levels involved in this experiment is shown in Figure 1.

When the  $z^3F_4^0$  sublevel is over populated by laser pulses tuned to the  $a^3F_4 - z^3F_4^0$  radiative transition (521.04 nm), we observe fluorescence light emission originating from the  $z^3F_j^0$  ( $j = 4, 3, 2$ ) sublevels. The time variation of the population density of the  $j = 4$  sublevel is studied by observation of the fluorescence light emitted in the  $z^3F_4^0 - a^3F_3$  transition (515.22 nm), to avoid signal perturbation by stray laser light. Population evolution of the  $j = 3$  and  $j = 2$  sublevels are analysed by observation of the sensitized fluorescence light emitted in the  $z^3F_3^0 - a^3F_3$  (519.29 nm) and in the  $z^3F_2^0 - a^3F_2$  (517.37 nm) radiative transitions respectively.

We observe that the relaxation curve shapes depend on the buffer gas (argon or neon) partial pressure, and on the auxiliary gas (hydrogen or nitrogen) partial pressure, but at fixed partial pressure values, no dependence has been detected on



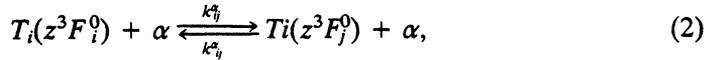
**Figure 1** Simplified diagram of the titanium levels involved in this experiment.

the discharge current intensity in all cases under study. This indicates, as in Ref. 1, that contributions of titanium atoms, rare-gas metastable states, atomic hydrogen or nitrogen and charged particles to the observed excitation transfer and quenching processes are negligibly small, according to their low concentration values in the region under study. Moreover, no fluorescence light emission has been detected originating from titanium levels other than the  $z^3F^0$  triplet state under study.

Consequently, in the laser-free regime, the laser induced population variations  $\Delta N_j$  ( $j = 4, 3, 2$ ) may be described by the following coupled rate-equation system:<sup>1</sup>

$$\begin{aligned} \frac{d\Delta N_4}{dt} &= -\Delta N_4 \left[ A_4 + \sum_{\alpha} (k_{43}^{\alpha} + k_{42}^{\alpha} + Q_4^{\alpha}) N_{\alpha} \right] + \Delta N_3 \sum_{\alpha} k_{34}^{\alpha} N_{\alpha} + \Delta N_2 \sum_{\alpha} k_{24}^{\alpha} N_{\alpha} \\ \frac{d\Delta N_3}{dt} &= -\Delta N_3 \left[ A_3 + \sum_{\alpha} (k_{34}^{\alpha} + k_{32}^{\alpha} + Q_3^{\alpha}) N_{\alpha} \right] + \Delta N_4 \sum_{\alpha} k_{43}^{\alpha} N_{\alpha} + \Delta N_2 \sum_{\alpha} k_{23}^{\alpha} N_{\alpha} \\ \frac{d\Delta N_2}{dt} &= -\Delta N_2 \left[ A_2 + \sum_{\alpha} (k_{24}^{\alpha} + k_{23}^{\alpha} + Q_2^{\alpha}) N_{\alpha} \right] + \Delta N_4 \sum_{\alpha} k_{42}^{\alpha} N_{\alpha} + \Delta N_3 \sum_{\alpha} k_{32}^{\alpha} N_{\alpha} \end{aligned} \quad (1)$$

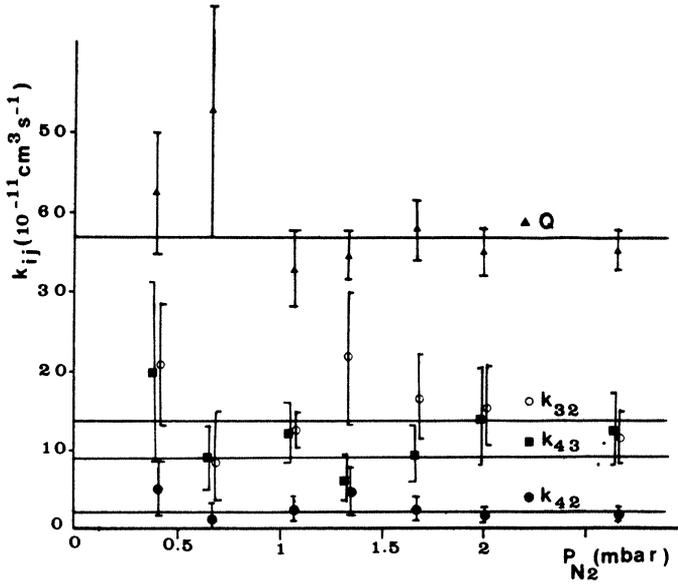
In Eq.(1),  $A_j$  represents the total radiative destruction probability of the  $j$ -sublevel (the medium is optically thin for the considered radiative transitions),<sup>1</sup>  $k_{ij}^{\alpha}$  and  $k_{ji}^{\alpha}$  are the forward and reverse rate coefficients of the reaction:



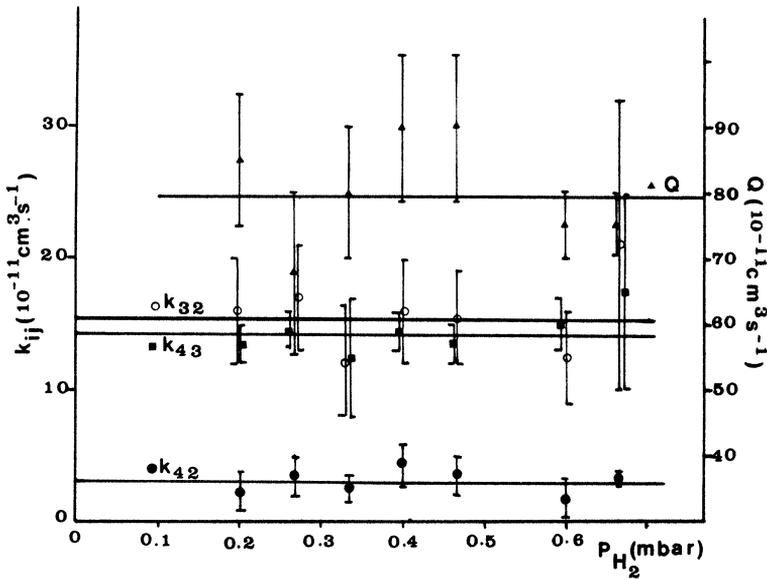
and  $Q_j^{\alpha}$  is the quenching rate coefficient of the  $j$ -sublevel by the  $\alpha$  collision partner of population number density  $N_{\alpha}$ .

Generally argon buffer gas is used for sputtering, at a partial pressure  $P_{Ar} = 0.8$  mb (measured in the observation chamber), corresponding to optimal conditions of titanium atoms production,<sup>1</sup> and we assume a complete mixing of the buffer gas and of the auxiliary gas directly injected into the observation chamber. Numerous experiments have been achieved to improve this assumption. In Eq. (1), we assume a linear superposition of the contributions of the  $\alpha$  collision partners. The validity of this assumption has been checked by changing argon buffer gas in neon buffer gas. At measurement accuracy, the same results have been obtained in both cases.

Nitrogen (respectively hydrogen) gas is injected into the observation chamber at a partial pressure  $P_{N_2}(P_{H_2})$ .  $P_{Ar}$  and  $P_{N_2}(P_{H_2})$  are controlled by measuring the total pressure  $P$ , and the respective argon gas and nitrogen (hydrogen) mass-flow rates. The relaxation curves of fluorescence light intensities originating from the  $z^3F_j^0$  ( $j = 4, 3, 2$ ) sublevels are analysed for each nitrogen (hydrogen) partial pressure  $P_{N_2}(P_{H_2})$ . Then the  $k_{ij}^{N_2}$  ( $k_{ij}^{H_2}$ ) and  $Q_i^{N_2}$  ( $Q_i^{H_2}$ ) rate coefficients are deduced from experimental relaxation curves, for each  $P_{N_2}(P_{H_2})$  partial pressure value, by the "identification" numerical method<sup>1,49,50</sup> using Eq. (1) and the  $A_i$ ,  $k_{ij}^{Ar}$ ,  $Q_i^{Ar}$  rate coefficients previously measured.<sup>1</sup>



**Figure 2** “Total angular-momentum transfer”  $k_{ij}^{N_2}$  and quenching  $Q_i^{N_2}$  rate coefficients obtained from the experimental results using the numerical “identification method,” as function of the nitrogen gas pressure  $P_{N_2}$ . Within the measurement accuracy,  $Q_4^{N_2} = Q_3^{N_2} = Q_2^{N_2} = Q^{N_2}$ .



**Figure 3** “Total angular-momentum transfer”  $K_{ij}^{H_2}$  and quenching  $Q_i^{H_2}$  rate coefficients obtained from the experimental results using the numerical “identification method,” as function of the hydrogen gas pressure  $P_{H_2}$ . Within the measurement accuracy,  $Q_4^{H_2} = Q_3^{H_2} = Q_2^{H_2} = Q^{H_2}$ .

In order to reduce the number of parameters, we assume that the  $k_{ij}^\alpha$  and  $k_{ik}^\alpha$  rate coefficients are related by the balance equation:

$$k_{ij}^\alpha/k_{ik}^\alpha = [(2j + 1)/(2i + 1)] \cdot \exp[-\Delta E_{ij}/k_B T], \quad (3)$$

Where  $E_{ij} = [E(z^3F_j^0) - E(z^3F_i^0)]$ ,  $k_B$  is the Boltzmann constant, and  $T$  is the gas kinetic temperature:  $T = 400 \text{ K} \pm 25 \text{ K}$ . The errors bars on the  $k_{ij}^\alpha$  and  $Q_i^\alpha$  are determined by varying the solutions of Eq. (1) within the experimental uncertainties on the measured relaxation curves.

As expected, no influence of the discharge current intensities on the calculated values is observed.

The inferred  $k_{ij}^\alpha$  and  $Q_i^\alpha$  are shown in Figure 2 and in Figure 3 for  $\alpha = \text{N}_2$  and for  $\alpha = \text{H}_2$ , respectively. The mean values of  $k_{ij}^\alpha$  and  $Q_i^\alpha$ , obtained by linear regression, from the results of Figure 2 and Figure 3, are summarized in Table 1.

**Table 1** Total angular-momentum changing and quenching rate coefficients for the  $z^3F_j^0$  ( $j = 2, 3, 4$ ) titanium sublevels induced by collision with hydrogen and nitrogen molecules in ground state, in units of  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

	$k_{43}^\alpha$	$k_{42}^\alpha$	$k_{32}^\alpha$	$Q_4^\alpha$	$Q_3^\alpha$	$Q_2^\alpha$
$\alpha = \text{H}_2$	$14.2 \pm 1.5$	$3.0 \pm 0.7$	$15.1 \pm 1.8$	$80 \pm 8$	$80 \pm 8$	$80 \pm 8$
$\alpha = \text{N}_2$	$9.2 \pm 1.5$	$2.2 \pm 0.5$	$13.2 \pm 1.6$	$37 \pm 4$	$37 \pm 4$	$37 \pm 4$

#### IV. DISCUSSION

Velocity-averaged cross sections  $\bar{\sigma}_{ij}^\alpha$  deduced from the  $k_{ij}^\alpha$  rate coefficients given in Table 1 are summarized in Table 2:

$$\bar{\sigma}_{ij}^\alpha = k_{ij}^\alpha/V, \quad (4)$$

where  $V = (8RT/\Pi M)^{1/2}$  is the thermal collision velocity,  $R$  is the ideal-gas constant,  $M$  the reduced mass of colliding partners, and  $T$  is the gas temperature ( $R = 400 \text{ K} \pm 25 \text{ K}$ ). For comparison, we have reported also in Table 2 the results previously obtained for titanium noble gas collisions.<sup>1</sup>

Due to the lack of other published measurements or theoretical calculations concerning the transition metals, the measured cross sections can be only discussed in relation with the results obtained for other materials, and particularly for alkali-metal atoms, though it would be probably not accurate to use simplified two state models to describe collision-induced "J-changing" process within a triplet state, even with structureless collision partner.<sup>51</sup> For comparison, results obtained for alkali-metal and other metal atoms are reported in Table 2.

*A—Total-angular-momentum changing ("J-changing") within the  $z^3F^0$  titanium excited state induced by collision with  $\text{N}_2$  and  $\text{H}_2$  molecules.*

Analysis of the published results on fine-structure transitions in alkali-metal atoms induced by collisions with  $\text{H}_2$  or  $\text{N}_2$  molecules, indicates that different behaviors are encountered according to the alkali-metal atom involved.

**Table 2** Velocity averaged cross sections for total angular momentum changing and for quenching of the  $z^3F_0^0$  titanium sublevels for collisions with nitrogen and hydrogen molecules. Comparison with available data. Cross sections in units of  $\text{\AA}^2$ .

Intramultiplet transfers						
Ti( $z^3F_i^0$ ) → Ti( $z^3F_j^0$ ) (this work)	$\Delta E_{ij}$ ( $\text{cm}^{-1}$ )	$\Delta E_{ij}/kT$	N <sub>2</sub>	Ar	H <sub>2</sub>	He
4 → 2	250	0.90	3.2 ± 1	3.1 ± 1	1.4 ± 0.5	1.7 ± 0.5
4 → 3	153	0.55	13.3 ± 2	11 ± 1	6.8 ± 1	11 ± 2
3 → 2	100	0.36	19 ± 2	14 ± 2	7.2 ± 1	7 ± 2
Quenching						
Ti( $z^3F_i^0$ ) $i = 4, 3, 2$ (this work)			53 ± 7	4.5 ± 0.6	38 ± 4	1.7 ± 0.4
Excitation transfers alkali-metals						
Li2 <sup>2</sup> P <sub>3/2</sub> → 2 <sup>2</sup> P <sub>1/2</sub> <sup>19</sup>	0.34	8.67 10 <sup>-4</sup>		53.1 ± 2.3	26.9 ± 1.4	37.3 ± 3.3
K4 <sup>2</sup> P <sub>3/2</sub> → 4 <sup>2</sup> P <sub>1/2</sub> <sup>26</sup>	57	0.24	54 ± 8		39 ± 6	
K4 <sup>2</sup> P <sub>1/2</sub> → 4 <sup>2</sup> P <sub>3/2</sub> <sup>25</sup>	-57	0.22	30 ± 3	19 ± 3	70 ± 20	32 ± 3
Rb5 <sup>2</sup> P <sub>1/2</sub> → 5 <sup>2</sup> P <sub>3/2</sub> <sup>29</sup>	-238	0.85	10 ± 5		7 ± 3	0.04
Rb6 <sup>2</sup> D <sub>3/2</sub> → 6 <sup>2</sup> D <sub>5/2</sub> <sup>32</sup>	2.26	9.3 10 <sup>-3</sup>	640 ± 100	530 ± 80		660 ± 100
Rb7 <sup>2</sup> D <sub>3/2</sub> → 7 <sup>2</sup> D <sub>5/2</sub> <sup>32</sup>	1.51	6.2 10 <sup>-3</sup>	1000 ± 150	1040 ± 160		880 ± 150
Rb8 <sup>2</sup> D <sub>3/2</sub> → 8 <sup>2</sup> D <sub>5/2</sub> <sup>32</sup>	1.01	4.1 10 <sup>-3</sup>	1210 ± 240	1240 ± 250		890 ± 140
Cs7 <sup>2</sup> P <sub>3/2</sub> → 7 <sup>2</sup> P <sub>1/2</sub> <sup>34</sup>	181	0.65	18		22	
Excitation transfers other metals						
Cd5 <sup>3</sup> P <sub>1</sub> → 5 <sup>3</sup> P <sup>02</sup>	565	1.83	8.0 ± 1.5	<2 10 <sup>-3</sup>	7.0 ± 1.5	
Cd5 <sup>3</sup> P <sub>1</sub> → 5 <sup>3</sup> P <sup>03</sup>	565	1.83	5.9 ± 0.9			
Ca <sup>3</sup> P <sub>1</sub> <sup>0</sup> → <sup>3</sup> P <sub>1</sub> <sup>09</sup>						
2 → 1	106	0.35			88 ± 25	31.9 ± 4.2
2 → 0	158	0.53			19.6 ± 1.3	5.5 ± 1.6
1 → 0	52	0.12			29.8 ± 45	2.0 ± 5.0
Quenching alkali-metals						
Li2 <sup>2</sup> P <sup>16,17</sup>	1400 K	23.9			18.4	
Li2 <sup>2</sup> P <sup>17</sup>	890 K	39.1 ± 0.8			24.3 ± 0.2	
Li2 <sup>2</sup> P <sup>19</sup>	564 K		53.2		40.7	37.2
Na3 <sup>2</sup> P <sup>20</sup>	900 K	22			8	
Na3 <sup>2</sup> P <sub>3/2</sub> <sup>23</sup>	beam	18				
	0.16 eV					
Cs7 <sup>2</sup> P <sup>34</sup>	400 K	160			65	
Quenching other metals						
Cd5 <sup>3</sup> P <sub>1</sub> <sup>2,3</sup>	443 K	(2.96 ± 0.4)10 <sup>-2</sup>			11.0 ± 0.5	
Cd5 <sup>1</sup> P <sub>1</sub> <sup>2</sup>	443 K	48.5 ± 5	1.1		19 ± 2	
Zn4 <sup>1</sup> P <sub>1</sub> <sup>6</sup>	483 K	26			12	
Zn4 <sup>3</sup> P <sub>1</sub> <sup>6</sup>	583 K	4.4			21	
Pb6p7s( <sup>3</sup> P <sub>1</sub> ) <sup>14</sup>	660 K	12.2 ± 1			0.31 ± 0.1	<0.2

On one hand, for light alkali-metal atoms, similar values of fine-structure changing cross sections are found for systems such as Li-He and Li-H<sub>2</sub> or Li-D<sub>2</sub> in cell,<sup>19</sup> K-He and K-H<sub>2</sub> or K-Ar and K-N<sub>2</sub> in beam experiment.<sup>25</sup> This suggests that the same mechanism is mainly responsible of the observed fine-structure changing process when induced by N<sub>2</sub> instead of Ar, or when induced by H<sub>2</sub> instead of He.

On the other hand, for heavier alkali-metal atoms, large differences are observed between alkali-metal—noble gas and alkali-metal—diatomic molecule systems such as Rb(5<sup>2</sup>P) H<sub>2</sub><sup>29</sup> and Cs(7<sup>2</sup>P) - H<sub>2</sub><sup>34</sup> corresponding to fine-structure energy splittings of 238 cm<sup>-1</sup> and 181 cm<sup>-1</sup>, respectively, close to the  $Ti(z_3F^0)$  values.

Experimental studies of fine-structure-changing transitions have also been carried out for collision of atoms in triplet states with molecular partners. In contrast to <sup>2</sup>P states, three distinct transitions are possible. These studies have involved principally the fine-structure-changing transitions in (Ca4s4p<sub>3</sub>P<sup>0</sup>) induced by collision with H<sub>2</sub> and D<sub>2</sub> molecules<sup>9</sup> and the <sup>3</sup>P<sub>1</sub>-<sup>3</sup>P<sup>0</sup> transition in Cd induced by collision with H<sub>2</sub>, N<sub>2</sub><sup>2,3</sup> and hydrocarbon molecules.<sup>5</sup> As for the heavy alkali-metal atoms, the intra multiplet mixing cross-sections are found larger with molecular collision partners than with rare gases.

The assumption of passage through an ionic complex A + X<sub>2</sub><sup>-</sup> (A is the metal atom and X<sub>2</sub> the molecule), may be introduced to explain the observed differences. The physical basis of such a model, is the observation that at internuclear distance R < R<sub>c</sub>, the wavefunction for A-X<sub>2</sub> may have a large contribution from ionic configuration A<sup>+</sup>X<sub>2</sub>. R<sub>c</sub> is estimated by locating the crossing of the covalent diabatic potential, usually assumed to be nearly constant, and the coulombic potential of the ionic state. In atomic units, R<sub>c</sub> ≈ 1/ΔW, where ΔW is the difference in energy of the two states A<sup>+</sup>X<sub>2</sub> and A<sup>+</sup>X<sub>2</sub><sup>-</sup>, as R → ∞.<sup>37,42</sup>

$$\Delta W = W_{\text{ion}}^* - E.A.X_2 \quad (5)$$

In Eq. (5), W<sub>ion</sub><sup>\*</sup> represents the ionization potential of the metal atom excited state A<sup>\*</sup>, and E.A.X<sub>2</sub> is the electronic affinity of the X molecule. The interaction of Cs(6<sub>2</sub>P) with N<sub>2</sub> has been discussed in terms of this mechanism in Ref. 39. The essential point of this model is that if the turning point of a given trajectory corresponds to a distance shorter than R<sub>c</sub>, the fine structure levels are completely mixed. The value of R<sub>c</sub> at which such ionic configuration contributes to the wavefunction is always smaller for systems involving H<sub>2</sub>, than for system involving N<sub>2</sub> according to their respective electronic affinity. For the Ti(z<sup>3</sup>F<sup>0</sup>)-H<sub>2</sub> and Ti(z<sup>3</sup>F<sup>0</sup>)-N<sub>2</sub> systems, we found R<sub>c</sub><sup>H<sub>2</sub></sup> = 3.4 a.u and R<sub>c</sub><sup>N<sub>2</sub></sup> = 4.2 a.u., respectively. Therefore these effects would be larger for collisions with N<sub>2</sub> than for collisions with H<sub>2</sub>. However, the model of Ref. 39 does not take into account the quenching processes, and presumably a large probability of quenching, as observed experimentally would lead to fewer fine-structure transitions.

Recently a new coupling mechanism has been suggested to be responsible for fine-structure transitions induced by molecular colliding partners.<sup>37,38</sup> This mechanism is a radial coupling located a rather close alkali-metal-molecule distance (R<sub>2</sub> ≈ R<sub>c</sub>), and is due to the anisotropy of the interaction. Calculations based on this model indicates that this new coupling is very important for the Rb(5P)-H<sub>2</sub> collisions and

less important for Rb(*5P*)–N<sub>2</sub> processes which is dominated by ions intermediate contribution. The results given by this model agree reasonably well with experimental data.<sup>29</sup>

Finally, electronic-to-rotational near resonant energy transfer have been frequently invoked to explain large enhancements of fine-structure-transition cross sections when induced by collisions with molecules instead of noble-gases by several authors<sup>5,6,26,27,34,36</sup> and their eventual contributions discussed by other authors.<sup>9,21,25,28–32</sup> Recent quantum-mechanical calculations<sup>45–47</sup> have bring clarifications on the near resonance phenomena. These calculations have shown that the strong isotopic effect observed the  $5^2P_{1/2} \rightarrow 5^2P_{3/2}$  transition in Rb–H<sub>2</sub> and D<sub>2</sub> collisions in a crossed beam experiment<sup>30</sup> is mainly due to a balance between the relative population of rotational levels and the relative importance of the transition cross sections as well as their energy dependance, rather than to near resonant electronic-rotation energy transfers. As suggested by the authors, these conclusions are not specific to the case of the  $5^2P_{1/2} \rightarrow 5^3P_{3/2}$  transition in Rb induced by collision with H<sub>2</sub> and D<sub>2</sub> but should be kept in mind when interpreting other experimental data.

*Collision with N<sub>2</sub>.* In contrast with the results obtained for the  $^3P_1$ – $^3P_0$  transition in Cd and for the heavy alkali–metal atoms, we observe immediately in *Table 2* that the measured “J-changing” cross sections are of the same order of magnitude when induced by argon or nitrogen colliding partners. This suggests that the same mechanism is mainly responsible of the observed “J-changing” process when induced by Ar or N<sub>2</sub>. By analogy with the results obtained for light alkali–metal atoms, this process may be presumably ascribed to a non-adiabatic radial coupling at a distance (*R*<sub>1</sub>) where the fine-structure interval  $\Delta E$  is equal to the splitting  $\Delta V$  between the attractive and repulsive potential curves emerging from the  $z^3F^0$  titanium state. In this case, *R*<sub>1</sub> is assumed to be large compared with the N–N separation in N<sub>2</sub> ( $\approx 1.1$  Å), N<sub>2</sub> has an atomic behavior, and the collision might be treated in the frame of a semi-classical theoretical approach,<sup>52</sup> provided the interaction potential curves was known.

If this interpretation seems to account for the measured  $z^3F_4^0 \rightarrow z^3F_2^0$  fine-structure transition cross section ( $\sigma_{42}^{N_2} \approx \sigma_{42}^{Ar}$ ), differences are observed for the two other transitions when the colliding partner is N<sub>2</sub> instead of Ar, despite the relatively large experimental uncertainties:

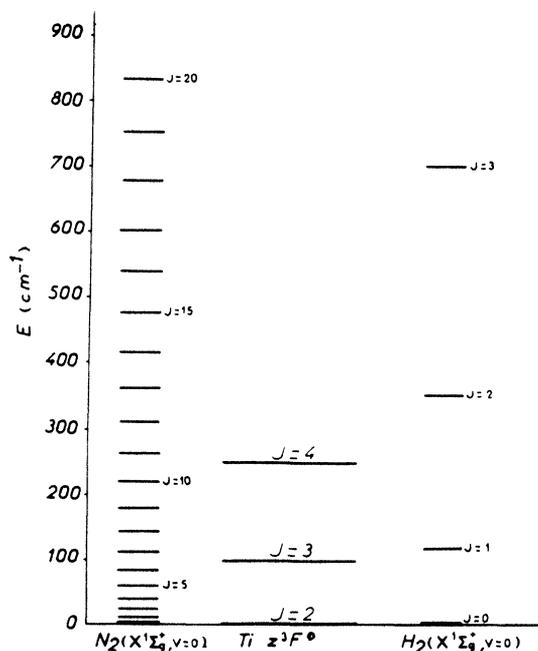
$$\bar{\sigma}_{43}^{N_2} - \bar{\sigma}_{43}^{Ar} \approx 2 \text{ \AA}^2; \bar{\sigma}_{32}^{N_2} - \bar{\sigma}_{32}^{Ar} \approx 5 \text{ \AA}^2$$

As previously quoted, passage through an ionic intermediate complex Ti<sup>+</sup> – N<sub>2</sub><sup>–</sup>, assumed to cause mixing of the fine-structure levels<sup>39</sup> or additional non-adiabatic coupling caused by the anisotropy of the molecule<sup>36,37</sup> might be invoked to explain these differences. However, we may expect that the effects of such phenomena are of the same order for the three “J-changing” processes under study, while measurements seem to indicate a correlation between the differences ( $\bar{\sigma}_{ij}^{N_2} - \bar{\sigma}_{ij}^{Ar}$ ) and the corresponding fine-structure energy splittings  $\Delta E_{ij}$ . This observation suggests that electronic-to-rotational near resonant and energy transfers may explain these differences.

Indeed examination of the partial energy diagram reported in Figure 4, shows that such near resonances exist between fine-structure energy splittings of the  $z^3F^0$  titanium excited state and rotational transitions with  $|\Delta J| = 2$  ( $J$  is the rotational quantum number) of nitrogen ground state molecule. In our experimental conditions (gas temperature = 400 K), only the  $\nu = 0$  vibrational state is significantly populated, and the relative population distribution ( $N_J = [N_2(X^1\Sigma_g^+, \nu = 0, J)]/[N_2]$ ) in the rotational levels is given in Figure 5. For the  $4 \rightarrow 2$  transition resonance phenomena, involving high-lying and consequently low-populated rotational levels ( $N_J \sim 0.01\%$ ), cannot contribute significantly to the measured value of  $\bar{\sigma}_{42}^{N_2}$ , while the contribution of these excitation transfer processes may be non negligible for the  $4 \rightarrow 3$  and  $3 \rightarrow 2$  transitions, according to the rather high relative population densities in the involved nitrogen levels,  $N_J \sim 2.5\%$  and  $N_J \sim 6.5\%$ , respectively.

However, the experimental error bars are too large to give definite conclusions on the eventual contribution of electronic to rotational near-resonant energy transfers.

*Collisions with H<sub>2</sub>.* Examination of Table 2 shows that fine-structure transitions, within the  $z^3F^0$  titanium excited state, have similar cross section values when induced by H<sub>2</sub> instead of isoelectronic helium noble-gas. As for collisions with nitrogen, this result contrasts with the fine-structure transition cross sections measured for heavy alkali-metal atoms and for the  $4s4p^3P^0$  triplet state of calcium<sup>9</sup> for which transition cross sections are found larger for H<sub>2</sub> and D<sub>2</sub> than for He collision partners (two or three times). The partial energy diagram of Figure 4 does not exhibit near-resonances between fine-structure titanium energy splittings and H<sub>2</sub> rotational



**Figure 4** Partial energy diagram of the rotational levels of the ( $X^1\Sigma + g, \nu = 0$ ) state of N<sub>2</sub> and H<sub>2</sub> molecules, and of the  $z^3F^0$  sublevels of titanium atom.

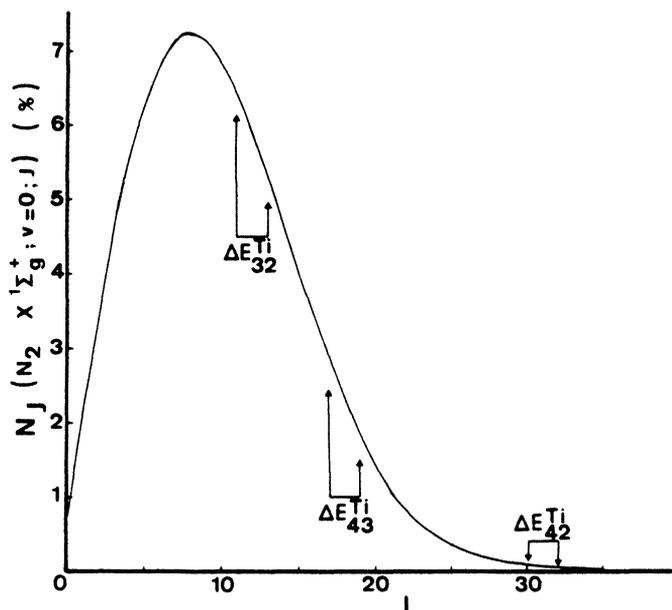


Figure 5 Relative population distribution in the rotational energy levels of the ( $X^1\Sigma + g, v = 0$ ) nitrogen molecule ground state.

transitions with  $\Delta J = 2$ , involving significantly populated  $H_2$  levels at gas temperature of 400 K. As for the Ti- $N_2$  system, these results suggest that the same mechanism is mainly responsible of the observed “J-changing” process when induced by He or by  $H_2$ . As done in the previous discussion, by analogy with the results obtained for light alkali-metal atoms, the observed processes may be presumably ascribed to non-adiabatic radial couplings at distances large compared to the H-H separation in  $H_2$  (0.74 Å).

### *B—Quenching of $z^3F^0$ titanium state by molecular colliding partners*

The quenching cross sections are found of the same order for the three  $z^3F_j^0$  titanium sub-levels under study for either  $N_2$  or  $H_2$  colliding partners, and considerably larger than for titanium noble gas systems. This observation agrees well with the results obtained for alkali-metal or other-metal atoms. Indeed, quenching processes by diatomic molecules have been much more extensively studied experimentally than “J-changing” induced by collisions, for Zn<sup>6,7</sup>, Cd<sup>2-5</sup>, Pb<sup>14</sup>, Li<sup>16,17</sup>, Na<sup>20</sup>, Rb<sup>31</sup>, Cs<sup>32</sup> and large cross sections values are generally found.

The model, that has been widely used to explain these large cross sections, is the “harpooning” or “curve crossing” mechanism.<sup>16,17,20,40</sup> According to this model, the upper state ( $A^*X_2$ ) potential energy surface intersects a strongly attractive surface of the ionic state ( $A^+X_2^-$ ), potential energy surface intersects the ground state ( $AX_2$ ). If the probabilities for jumping to the ( $A^+X_2^+$ ), and the ( $AX_2$ ) surfaces are large, the quenching cross section is related to the point at which the surfaces for ( $A^*X_2$ ) and

( $A^+X_2^-$ ) cross,<sup>17,20,40,42</sup> i.e. the  $R_c$  previously determined. However, a quantitative calculation of the quenching cross section must include all the potentials involved, i.e. the potential grid defined by  $A^*$  and vibrational levels of ground electronic state  $X_2$ , and a similar grid for ( $AX_2$ ) and ( $A^+X_2^-$ ). Such a model of successive non-adiabatic transitions from the incoming covalent curve to the ionic curve and then to the other covalent curve which correlates with final metal atom state, has been developed in Ref. 40 to explain quenching of Na excited states induced by collisions with  $N_2$  molecules. This approach neglects the orientation effects of the molecule during the collision process and has been partially improved by diatomics-in-molecules potential energy surfaces calculations.<sup>35</sup> However recent ab initio calculations of Na- $N_2$ <sup>43</sup> and Na- $H_2$ <sup>42</sup> systems, within the adiabatic framework, show that the adiabatic potentials exhibit a strong anisotropy, and that the observed transition can be explained by a single non-adiabatic transition at the crossing between the ground and the excited state. Pseudopotential molecular-structure calculations for all the alkali-metal- $H_2$  systems have been recently performed for ground and numerous excited state in  $C_{\infty v}$  and  $C_{2v}$  symmetries, and the results indicate that it might be audacious to use data for the A-He systems in order to interpret non-reactive A- $H_2$  collision processes.<sup>44</sup>

Moreover, reactive channels:



may contribute to the observed quenching processes.

Indeed, such processes have been studied both theoretically and experimentally for systems like  $Mg(^3P) + H_2$ ,  $D_2$ ,<sup>12,13</sup>  $Zn(^3P) + H_2$ ,  $D_2$ ,  $HD$ ,<sup>8</sup>  $Cs(^7P) + H_2$ ,<sup>33,35</sup> and for this last system a recent ab-initio diabatic approach of the reactive collision<sup>48</sup> supports the contribution of 'harpooning' mechanisms involving an ionic very flat ( $Cs^+H_2^-$ ) channel, which goes smoothly to the product valley  $CsH + H$ , the ground state of  $CsH$  being essentially ionic ( $Cs^+H^-$ ). Since the low-lying levels of the  $TiN$  molecule have an ionic character too,<sup>53</sup> the reactive channel (6) may be also invoked to contribute to the observed quenching processes. However the endothermicities of reactions (6), 2.46 eV for  $Ti^* + N_2$  and 0.48 eV for  $Ti^* + H_2$ , indicate that reactive channels are energetically possible only when the molecule involved in the collision is in an excited state (vibrationally excited states  $v > 1$  for  $H_2$  and  $v > 9$  for  $N_2$ ). In our experimental conditions population densities on these excited states are weak and consequently contribution of reactive channels is probably negligible.

According to the lack of information on  $TiH_2$  and  $TiN_2$  potential surfaces, we can just speculate on the basis of the results discussed above and suggest that the "harpooning" process may explain the large values of the measured quenching cross sections.

## V. CONCLUSIONS

Fine-structure changing collisions and quenching involving the triplet  $z^3F^0$  titanium excited state and diatomic molecules ( $H_2$ ,  $N_2$ ) have been studied by laser-perturbation and time-resolved spectroscopy, in the same experimental device as in Ref. 1.

Unfortunately the lack of available data on transition elements does not provide quantitative comparisons of our results with experimental or theoretical works of others. However, a qualitative comparison has been done with our previous measurements on titanium–noble-gas collisions, and with results published on alkali–metal–molecule systems and on group II.A and group II.B atom–molecule systems. From this comparison, we can only suggest that quenching is probably dominated by “harpooning” processes, and that fine-structure transitions within the  $z^3F_j^0$  titanium excited state induced by  $N_2$  and  $H_2$  behave similarly to the same processes in light alkali–metal atom–diatomic molecule systems. Particularly the cross section values are found of the same order when induced by  $N_2$  and Ar or when induced by  $H_2$  and He in contrast with the results published on heavy alkali–metal atoms and of triplet states of group II.A and group II.B atoms for which large differences are observed. This indicates that the process proposed by Hickman to explain the measured Rb fine-structure transitions induced by collision with  $N_2$  and  $H_2$  is probably unefficient in the case under study.

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