INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

SPECTROSCOPY OF TRANSITION REGION SPECIES

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REAGENT EXCITATION

LIF

$A + BC \rightarrow ABC \rightarrow AB + C$

TRANSITION REGION SPECTROSCOPY

"SIMULTANEOUS" Collisions

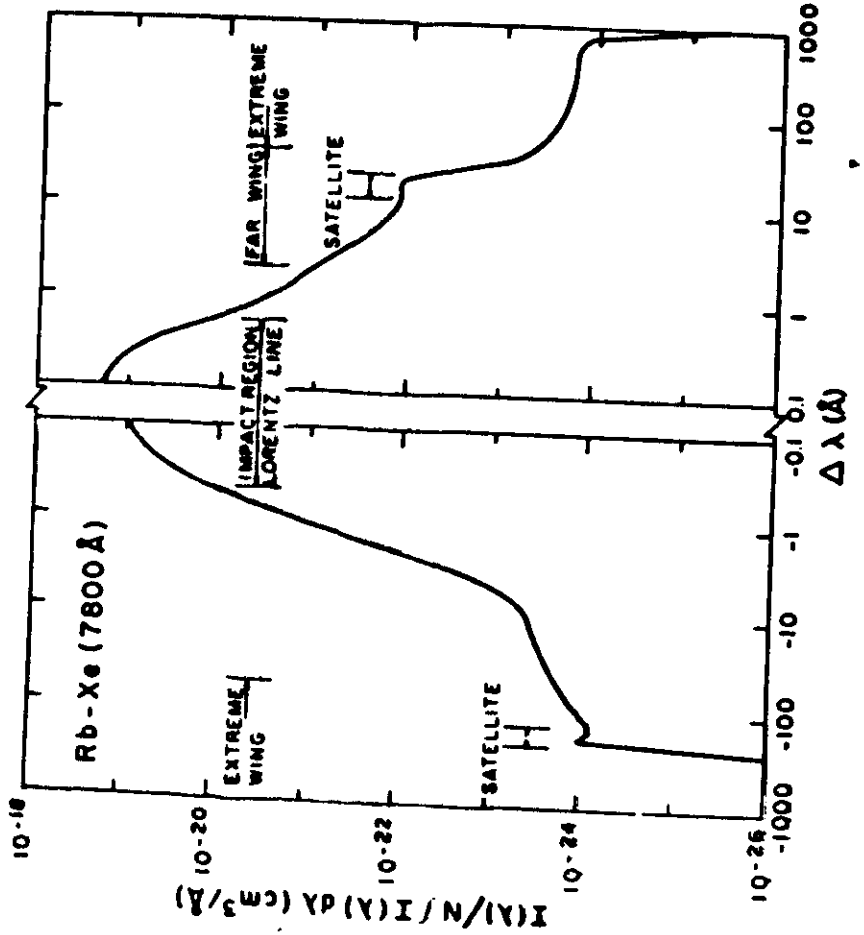
$A + BC + h\upsilon$

EXAMPLES

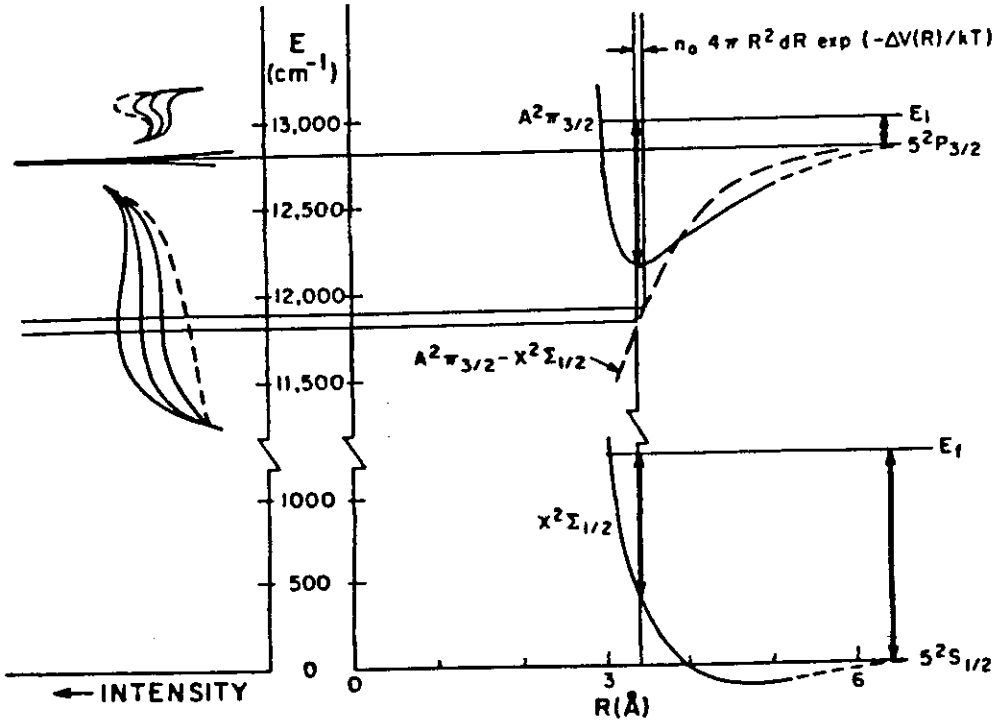
1) $Rb + Xe + h\upsilon$ - "LINE BROADENING"

2) $Sr + Ca + h\upsilon$ - "LICET"

3 $K + NaCl + h\upsilon$ - "TRS"

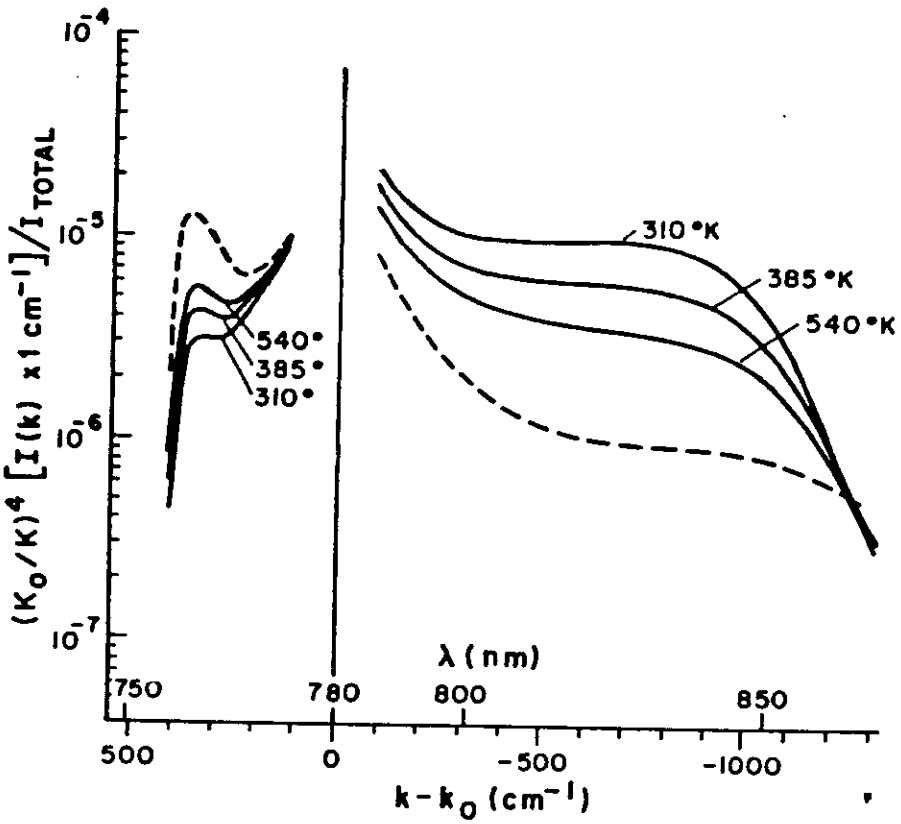


;. 3. Normalized emission spectrum of the Rb 7800Å D-line per-
:bed by xenon at $10^{19}/cm^3$ density. The gas temperatures in °K
: indicated. From Ref. 2.



g. 4. The model used to interpret the extreme-wing spectra in
g. 3, based on the classical Franck-Condon principle.

ALAN GALLAGHER



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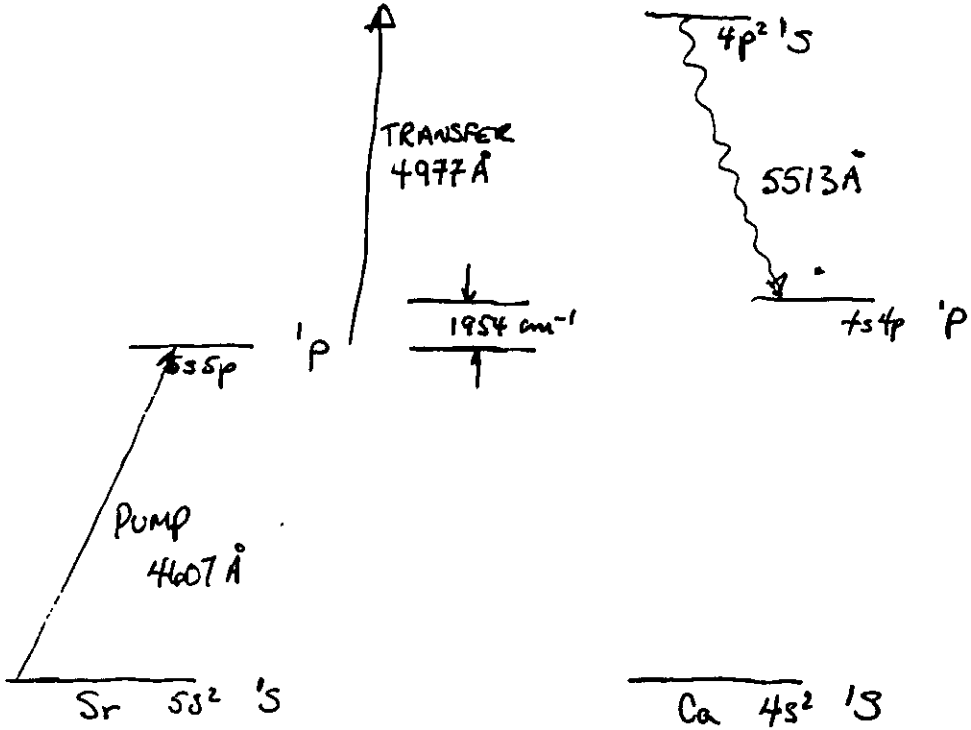
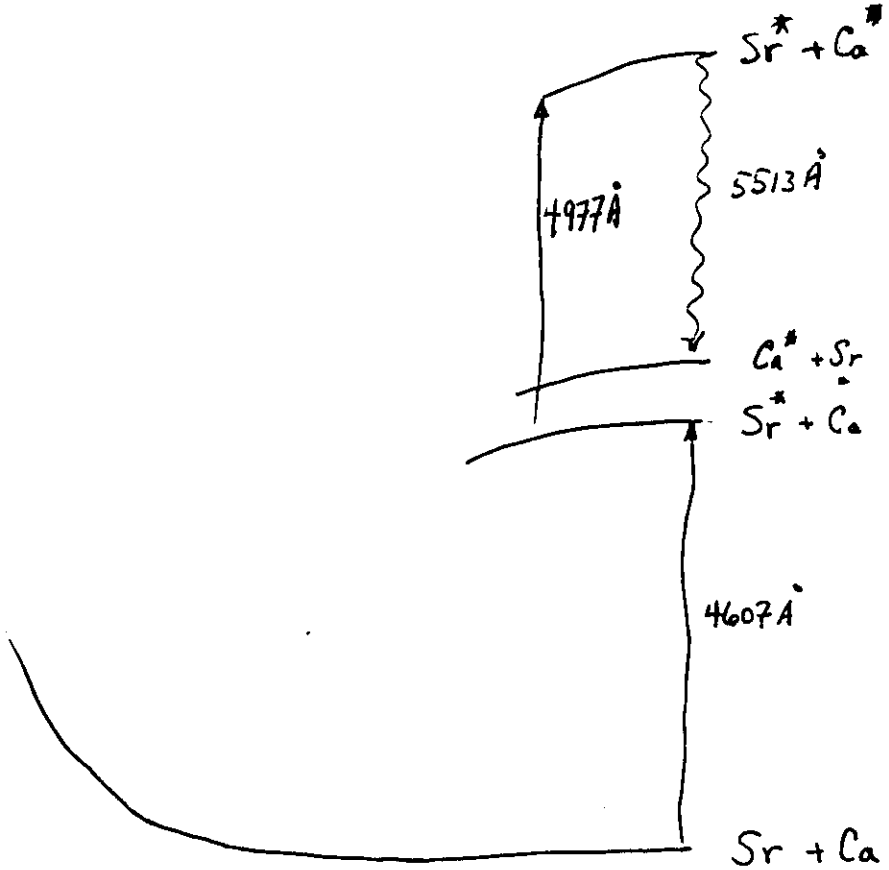

TRANSFER
4977 Å
1954 cm⁻¹
5s5p ¹P
PUMP
4607 Å
Sr 5s² ¹S
4p² ¹S
5513 Å
4s4p ¹P
Ca 4s² ¹S


Sr* + Ca*
4977 Å
5513 Å
Ca* + Sr
Sr* + Ca
4607 Å
Sr + Ca

V. Powerful Method - LIF

Zare, Dagdigian + Cruse :

$Ba + HCl \longrightarrow BaCl + H$ ... Fig 4 - Scheme
5 - Scheme

Smith & Zare Fig 1, 4

~~[illegible]~~

Complex formed, but NOT equilibrated

$\gamma \sim 1$ ps (Goes against theories which say all equilibrated in 10^{-13} sec)

Kinsey - Laser Doppler ?

Karny & Zare - Laser Preparation + Laser Probe

$(CaSr) + HF$, DF Fig 1, 4

Determine BDE of CaF, SrF (10^4 enhancement)

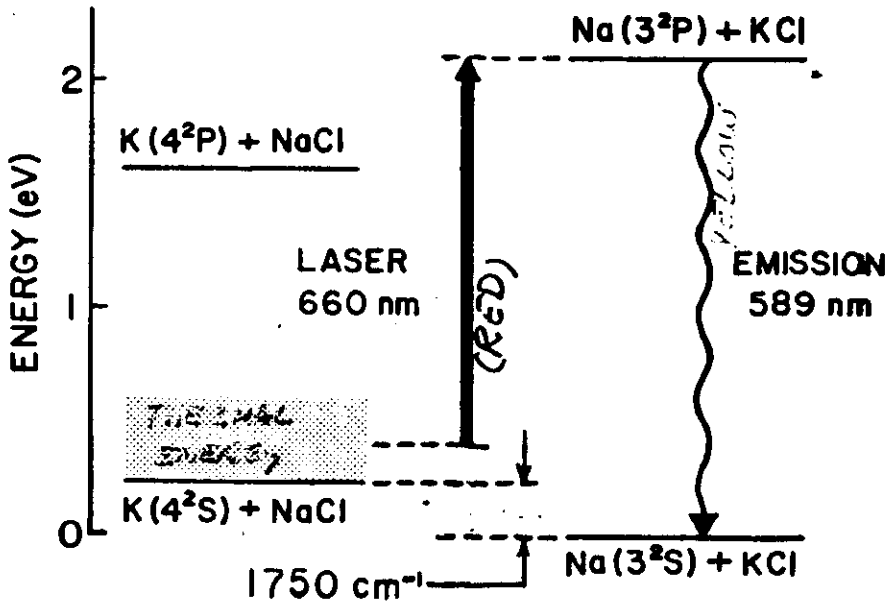
Energy Deposit - $f_v \sim 30, 40\%$

EXPERIMENTAL CRITERIA

1. FORMATION

2. DETECTION

3. INTERPRETATION


Na(3²P) + KCl
2
K(4²P) + NaCl
ENERGY (eV)
LASER
660 nm
EMISSION
589 nm
1
K(4²S) + NaCl
0
Na(3²S) + KCl
1750 cm⁻¹

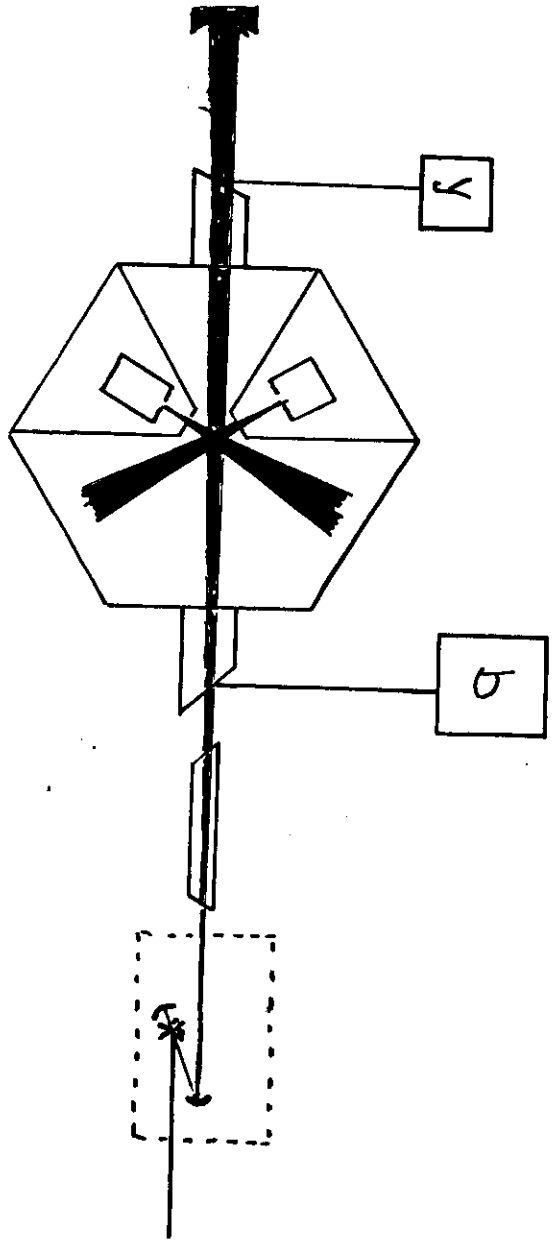
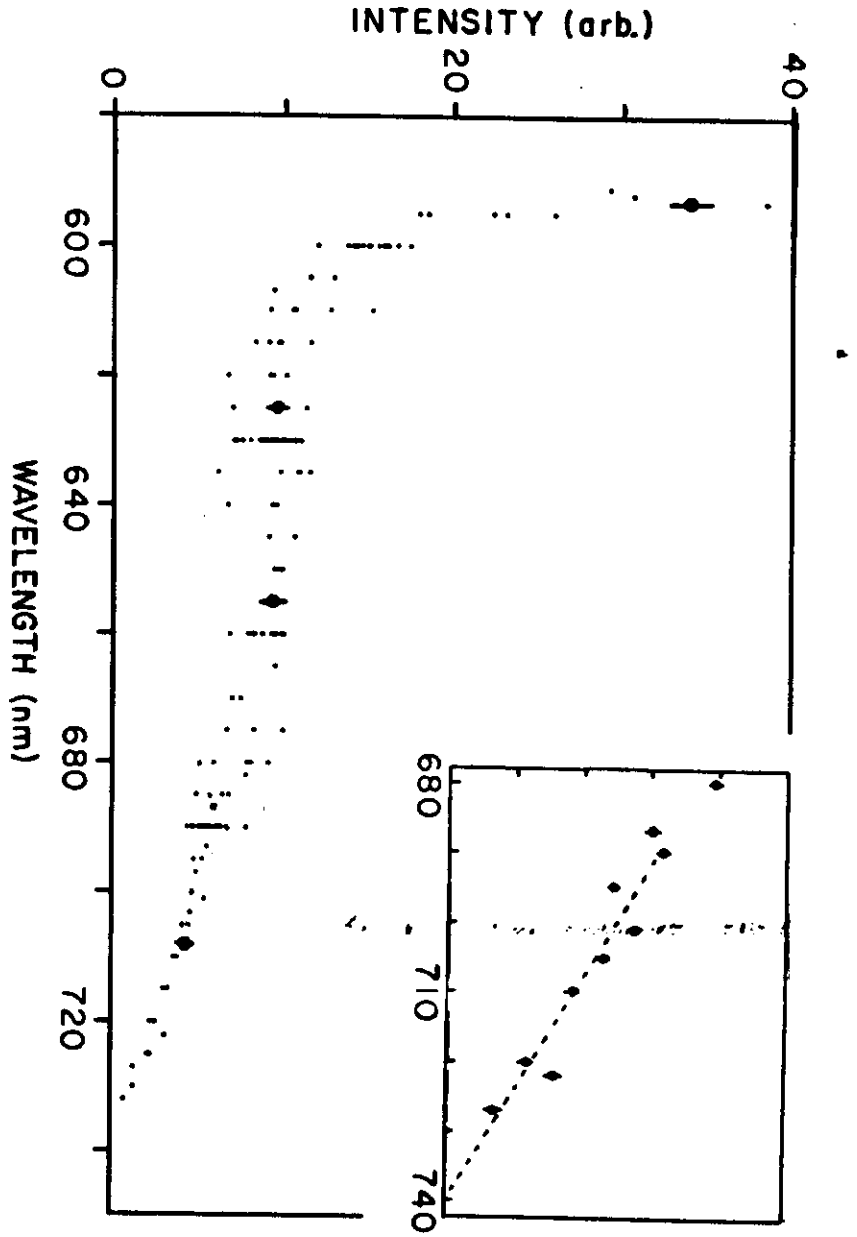
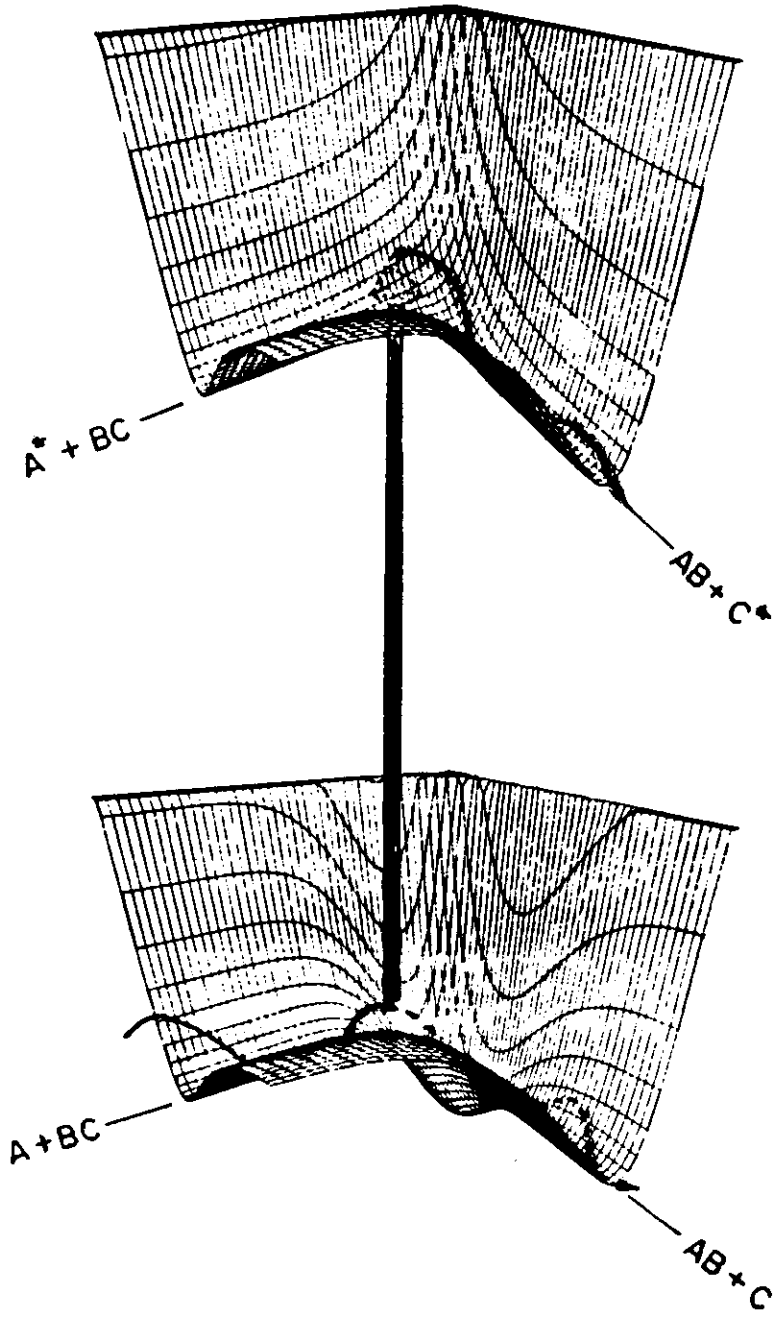

σ

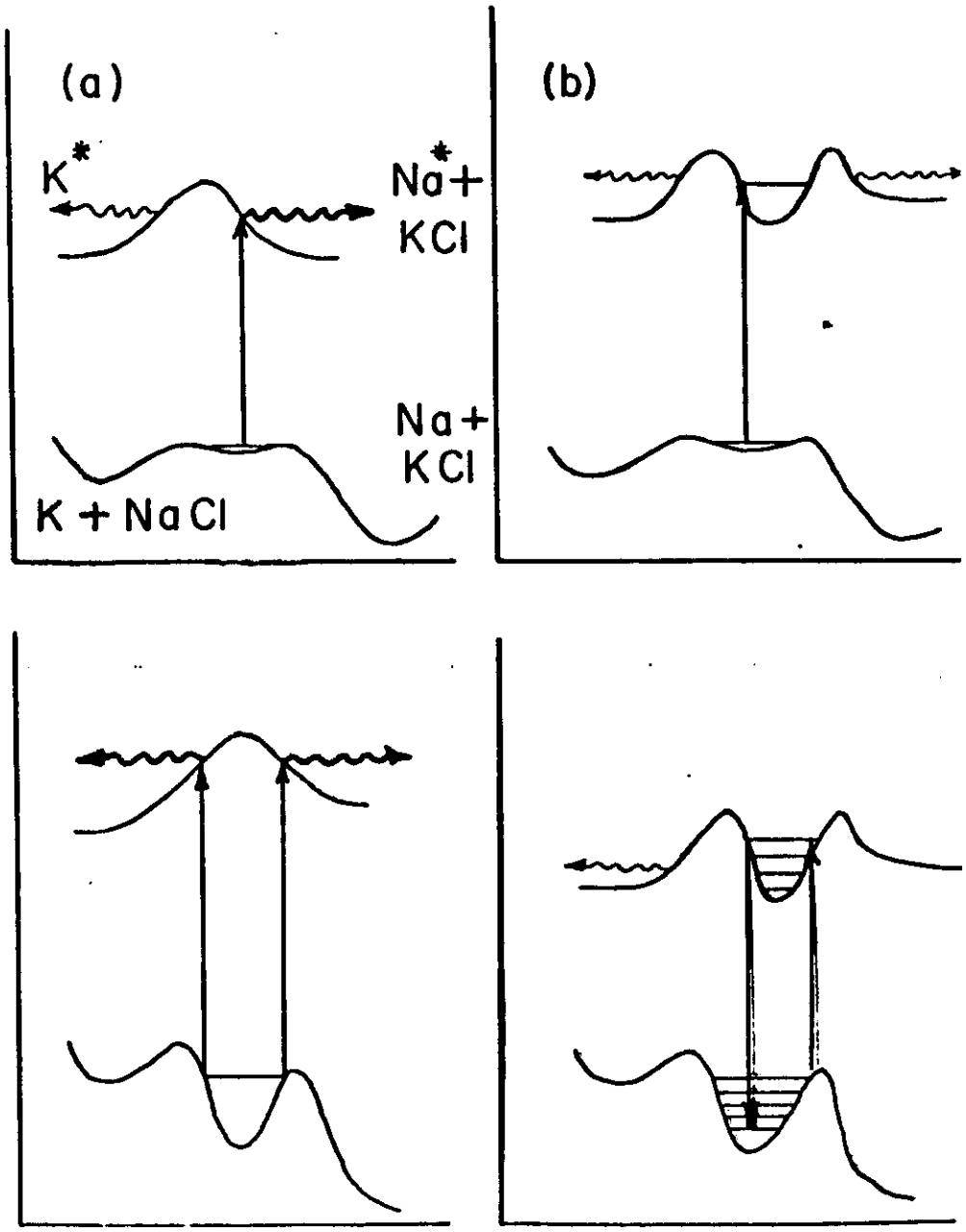
Table VI

Count rates (± 1 σ) for observation of Na-*D* radiation with various combinations of K, NaCl, and light beams for irradiation at $\lambda = 670$ nm.

Signal	Origin (Elementary Process)	Count rate (sec^{-1})
R_{000}	Dark Current	2.4 ± 1
R_{001}	Scattered Light	30.2 ± 2
R_{100}	K Background	2.7 ± 1
R_{010}	NaClBackground	7.0 ± 1
R_{101}	K Photoluminescence	169.7 ± 6
R_{011}	NaCl Photoluminescence	44.6 ± 4
R_{110}	Chemiluminescence	7.0 ± 2
R_{111}	Three-beam signal	481.5 ± 12




A* + BC
AB + C*
A + BC
AB + C

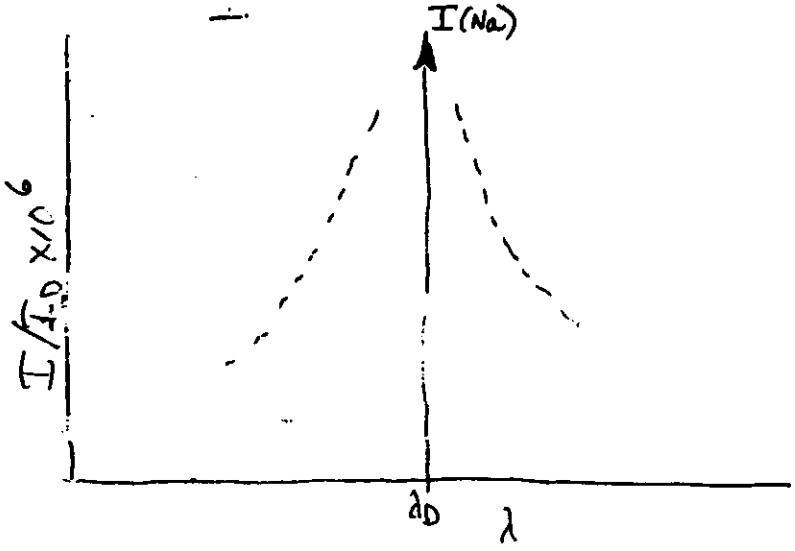

(a)
K*
Na* +
KCl
Na +
KCl
K + NaCl
(b)

$F + Na_2 \rightarrow NaF + Na^*$

$\tau_{rad} \sim 10^{-8}$

$\tau_{coll} \sim 10^{-12}$

$\frac{I_{complex}}{I^*} \sim 10^{-4}$



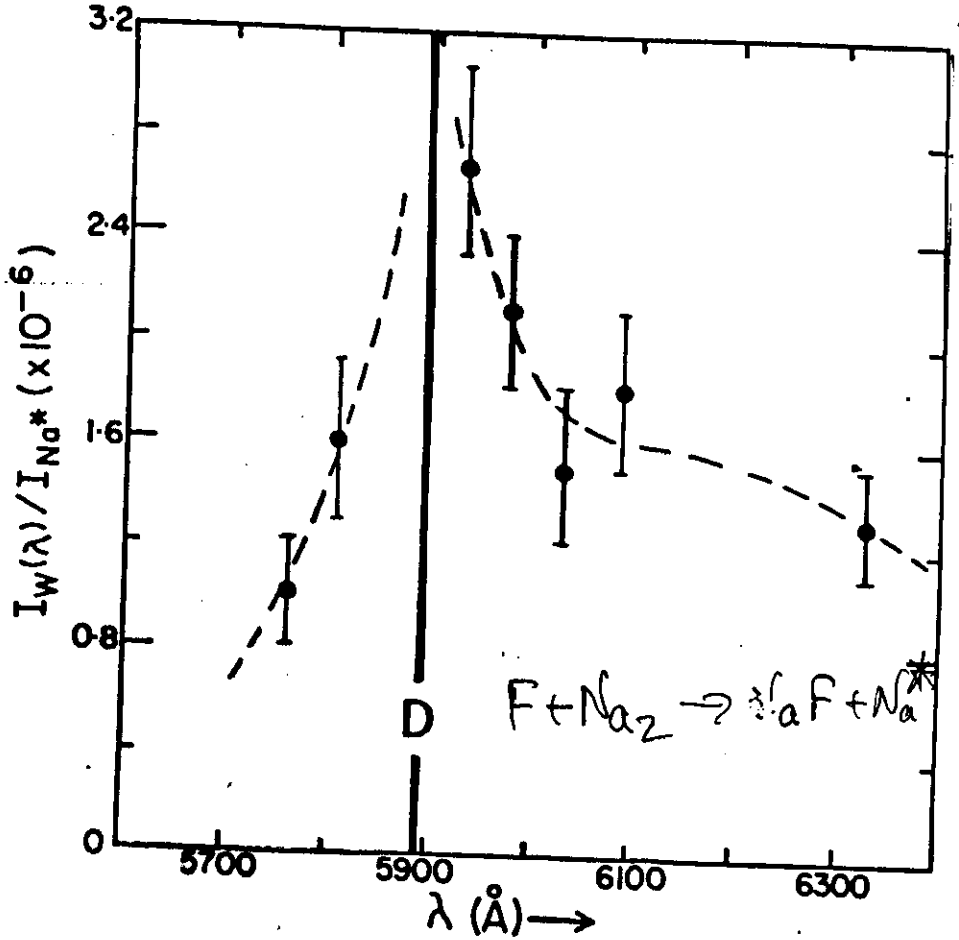
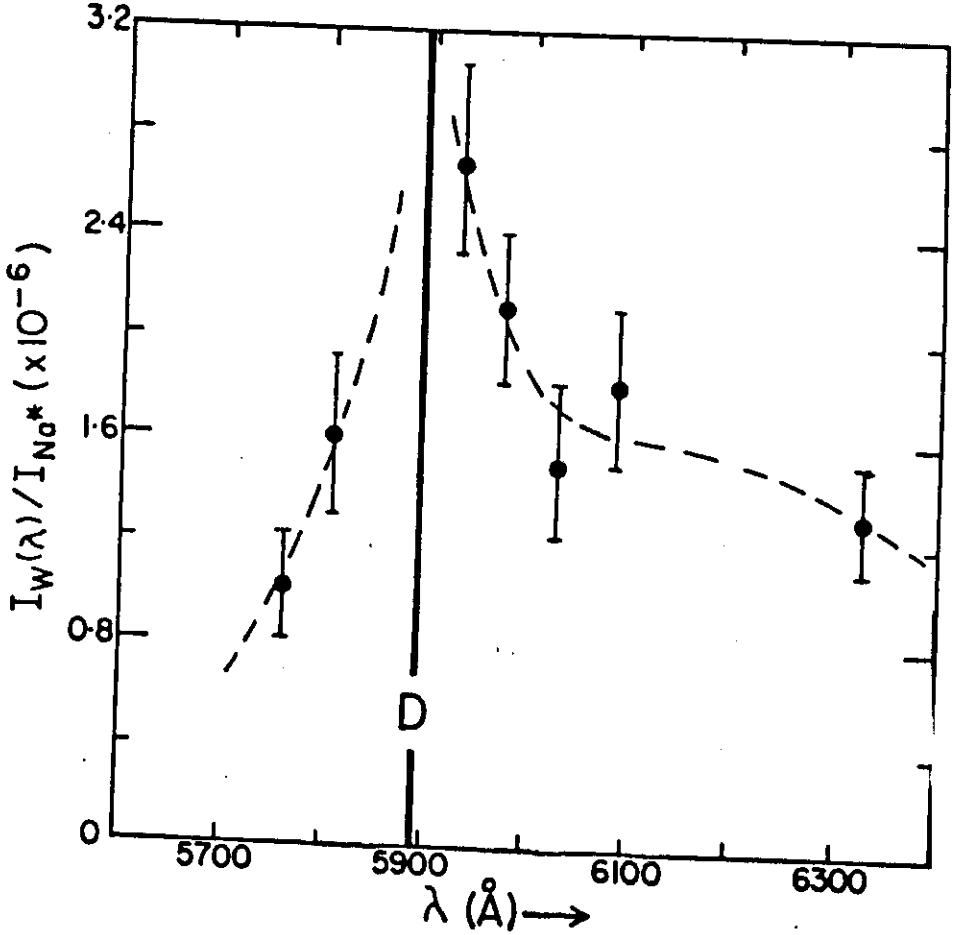


FIG. 1. Wings of the sodium *D* lines ($D_2 = 5890$ Å, $D_1 = 5896$ Å) recorded at a $D_2 + D_1$ intensity $I_{Na^*} = 2.4 \pm 0.2 \times 10^6$ counts/sec. Each point on the wing represents ~300 counts repeated once or twice; error bars give ~1σ deviation. Intensities were corrected for instrument sensitivity.

395-03$01.00



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95-03$01.00

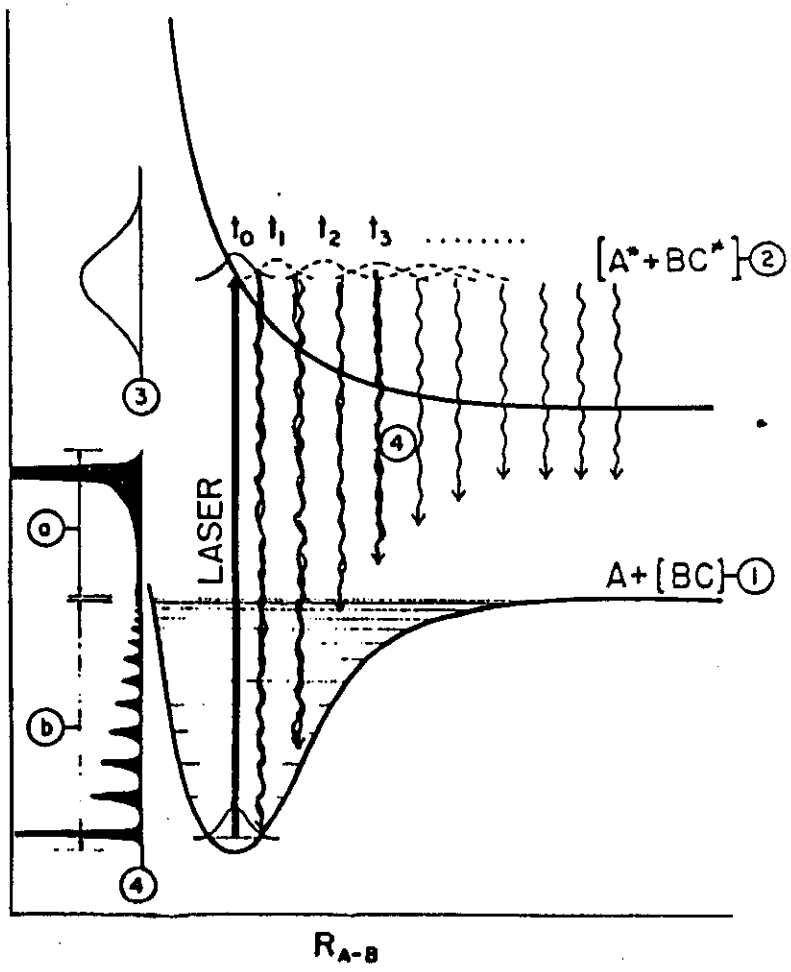

Figure 2. A photodissociation experiment. The laser transfers the ground-state wave function to the repulsive excited state where it evolves (dashed wave packets t_1, t_2, ..., etc.) into $A^* + BC^!$. Indicated in the figure by numbers are accessible experimental probes: (1) equilibrium geometry and spectroscopic constants of the final BC product, (2) internal-state, angular, and velocity distributions of the final products, (3) absorption (photodissociation) spectrum, (4) emission spectrum, (a) wing emission, (b) discrete emission.

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Chemical Dynamics Studied by Emission Spectroscopy of Dissociating Molecules

Dan Imre, James L. Kinsey,* Amitabha Sinha, and John Krenos†

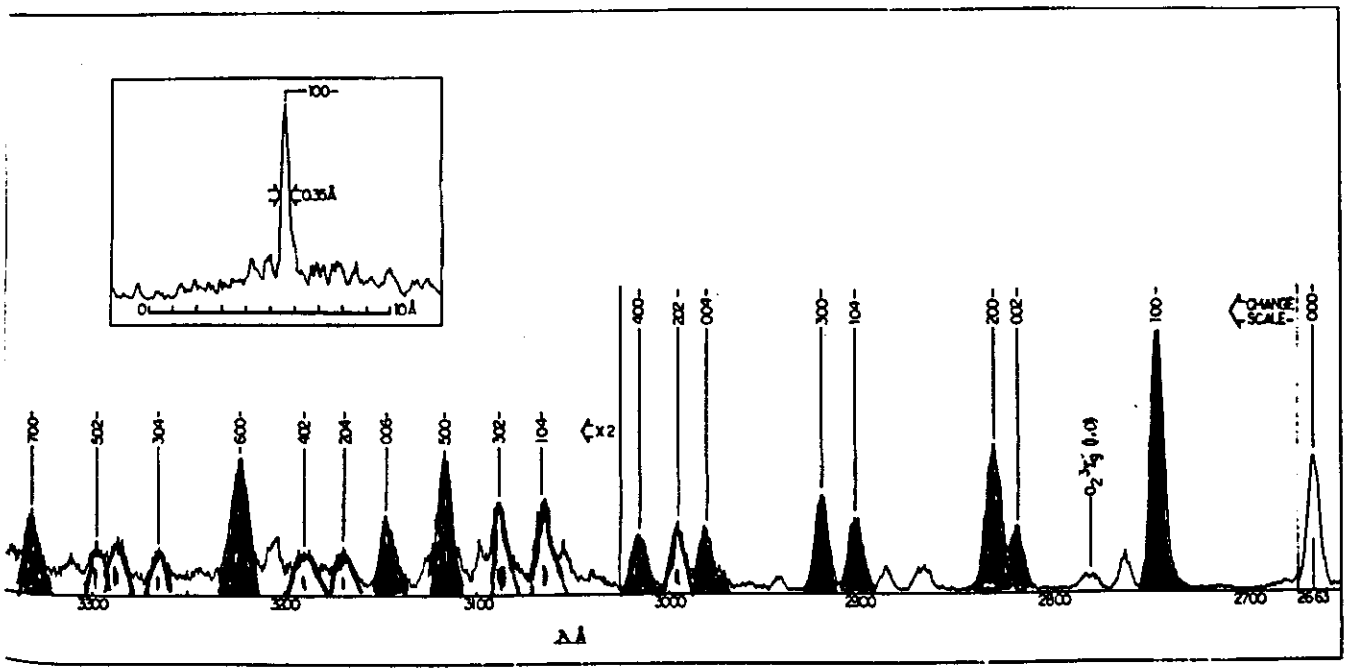
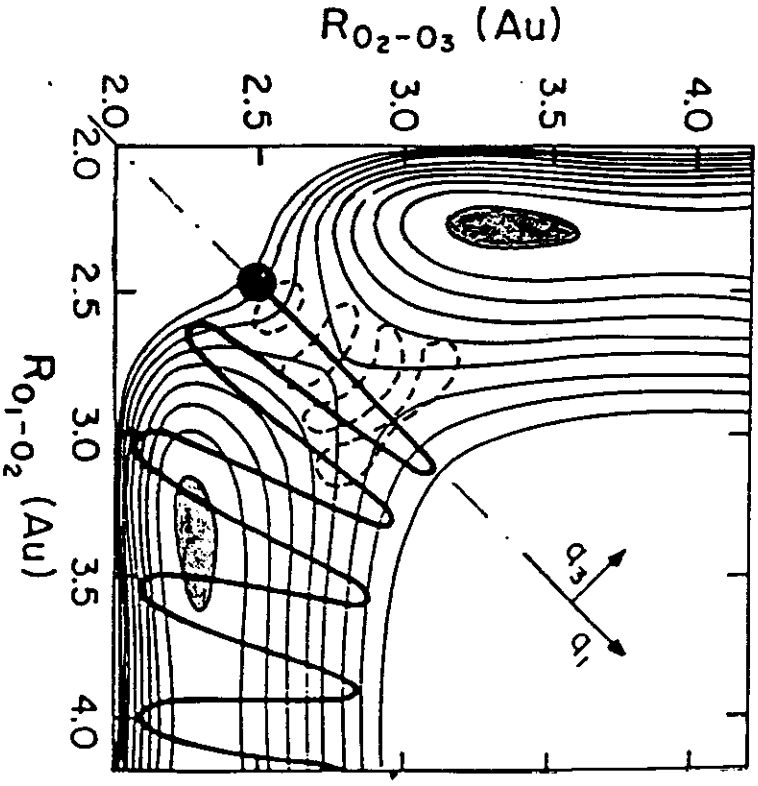


Figure 12. Ozone Raman spectrum obtained by exciting at 266 nm. Bands are labled ν_1, ν_2, ν_3. The insert is a higher resolution scan of the first band (100).



ure 13. Ozone B_2 excited-state surface along the two stretch coor-ates (q_1 and q_2), with the bending coordinate fixed at the ground-state :: (reproduced from ref 22). A photodissociation trajectory is shown :: wavy line. The spreading wave packet is in dashed lines. The gray :: indicate the quasi-bound regions in the exit channels.

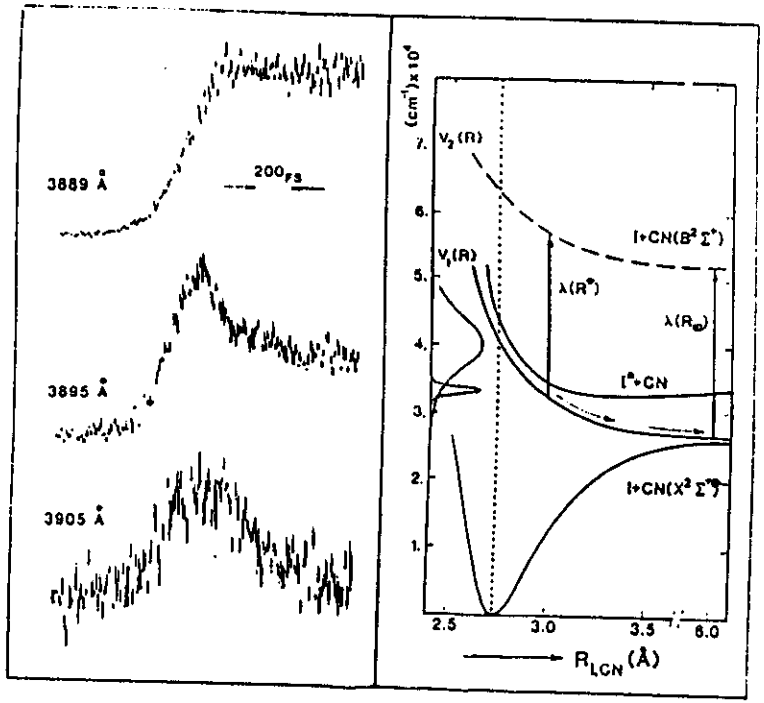


FIG. 1. (Right) Schematic for femtosecond probing of the transition state using a pump–probe (t, λ tuning) method. The PES are drawn to indicate the different probe wavelengths at "free" and "perturbed" CN transitions. The band on the vertical axis is the absorption spectrum (Ref. 18), and the profile of our pulse (shaded). The difference in $\lambda(R^*)$ and $\lambda(R_\infty)$ is not to scale, and the vdW wells are not shown. Note λ (R^*) spans the different ranges of R (see the text). (Left) Femtosecond transients at the different probe wavelengths indicated. The time scale is also displayed. More detailed analysis (see Ref. 19) will be given later (Ref. 13). The experimental conditions are given in text, and these transients (each displayed on a different scale) were obtained under identical conditions except for tuning of the wavelength. The coherence time and autocorrelation traces were obtained after each scan.

Real-time femtosecond probing of "transition states" in chemical reactions[a)]

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J. Chem. Phys. 87 (4), 15 August 1987

Collings, Polanyi, Smith, Stolow & Tarr

$$\vec{H} + D_2 \rightarrow HD_2^{\neq}$$

($\vec{H}$ from photolysis of H_2S @ 248 nm)

$$HD_2^{\neq} + h\nu_2 \rightarrow HD_2^{\neq *}$$

$$HD_2^{\neq *} + h\nu_2 \rightarrow HD_2^{+} + e^-$$

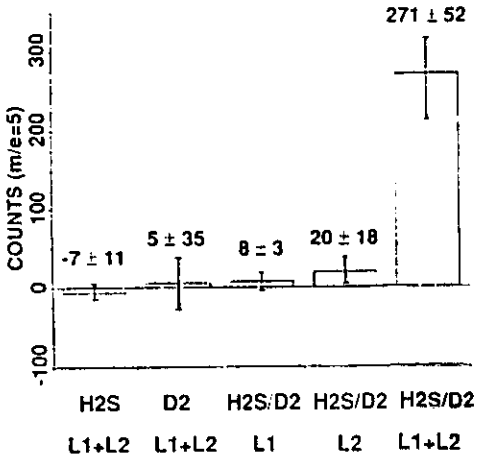

FIG. 1. Typical counting rate at $m/e=5$ (HD_2^+) per 5000 laser shots. L1 and L2 indicate the presence of the pump (248 nm) and probe (193 nm) laser radiation, respectively.

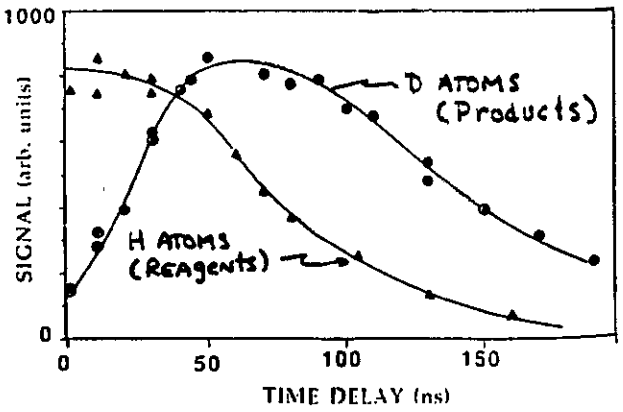

FIG. 2. H atom reactants (triangles) and D atom products (circles) in the chemical reaction $H+D_2$ as a function of pump-to-probe delay time.

Collings, Polanyi, Smith, Stolow + Tarr

$H + D_2 \longrightarrow HD_2^*$

$HD_2^* + h\nu \longrightarrow HD_2^* + h\nu \longrightarrow HD_2^+ + e^-$

Observation of the Transition State HD_2 in Collisions, $H+D_2$

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Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1
(Received 28 September 1987)

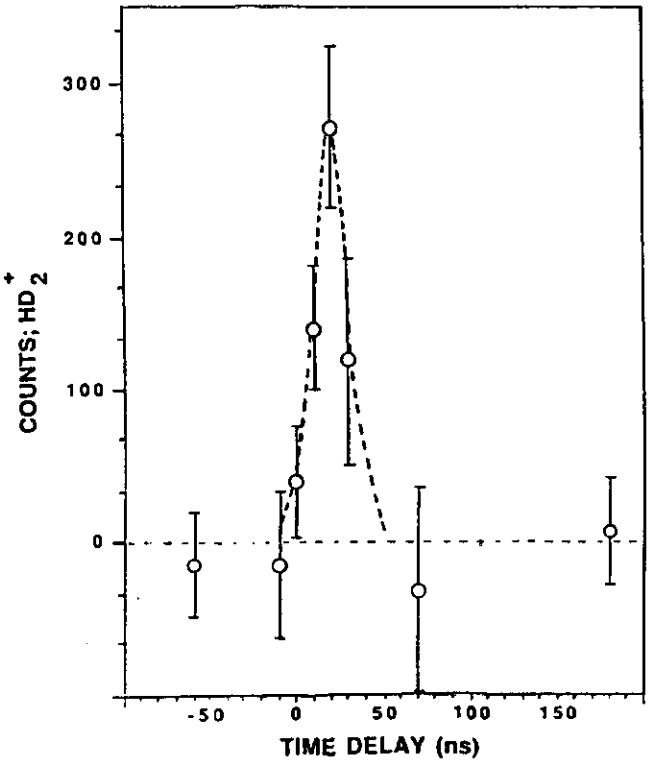

FIG. 3. The signal (counts per 5000 laser shots) at $m/e=5$ (HD_2^{+*}) as a function of pump-to-probe delay time. The dashed line is the quantity $R_f=k[H(t)][D_2]$ obtained from Fig. 2, normalized to the peak counting rate in Fig. 3.