STIMULATED PROCESSES IN A HALF-COLLISION

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Selective photodissociation of diatomic molecules is
used to prepare the separating species in a well de-
fined quantum state with narrowly determined final
kinetic energy of the particles. During the course of
separation to products the repulsive potential is
probed by a tunable dye laser, that is by induced ab-
sorption in case the dissociation proceeds on a poten-
tial leading to ground state products, or by induced
emission or absorption for all other cases. The de-
termination of interatomic potentials from the obser-
ved spectra is discussed.

1. INTRODUCTION

The probing of atomic and molecular interaction potentials

during collisions by means of laser techniques has become

more and more a common method. It has been shown that

"clean" collision parameters may be essential in the experi-

ments and for the interpretation of their results. Such

conditions can be realized in the photodissociation process

where initial conditions are in general well known, and the

problem is restricted to the treatment of only half a col-

lision. The observation of weak wing emission from an elec-

tronically excited dissociation product allows to deduce

information on the interaction potentials of both upper and
lower molecular states. This has been discussed in recent
years; see e.g. Foth et al.[1] and Telle[2].

Most experiments undertaken so far have been performed
in a vapor cell. This poses a severe drawback in many occa-
sions since evaporation temperatures for various molecules
may be quite high, and thus a large number of initial states
is populated. A more favorable condition is often found in
molecular beam experiments in which by seeding of the in-
vestigated molecule its vibrational and rotational tempera-
tures may be lowered significantly. Usually high densities
of the species are required since the signals to be observed
are extremely feeble; thus a high density beam source[3] has
to be used.

A further increase in sensitivity over pure emission
wings during the dissociation process is to be expected when
stimulated processes are utilized. Absorption of laser ra-
diation during atom-atom collisions is now well established
for probing their interaction potentials. For the dissocia-
tion along a potential curve leading to excited state pro-
ducts strong emission may be induced to the ground state
when sweeping the wing spectrum with a tunable laser; this
process can be viewed as being similar to stimulated Raman
scattering, and the induced transition is then evident as a
decrease of line intensity in the atomic product. The
streight-forward analogy to the absorption during an atom-
atom collision is encountered for absorption during the
dissociation process, but now only a half-collision has to
be treated. Successful absorption is detected as emission
from an excited product state.

The scheme is exemplified for the alkali halides. In
section 2 the principles are outlined how to derive   in-

termolecular potentials, for the case of atom-atom colli-
sions. Induced absorption and emission during the photodis-
sociation process are described in section 3, followed by
the discussion of some preliminary results in section 4.

2. PRINCIPLES OF ATOM-ATOM COLLISIONS

One elegant approach for the understanding of what is hap-
pening during the course of a collision is the absorption in
the (unbound) complex of close encounter in atom-atom scat-
tering. The interaction of the complex with a photon may
be described by

$$A + B + h\nu \;\rightleftarrows\; AB^{*\dagger} \rightarrow (\, A^{*} + B\,) \quad . \tag{1}$$
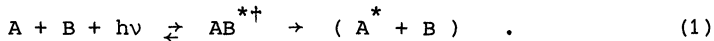
In general, the channel indicated parenthetically repre-
sents a minor pathway.

   The absorption of a photon during the collision, assu-
ming only vertical transitions in the classical Franck-Con-
don or quasistatic picture, probes the potential difference
$\Delta U = U^{*}(R) - U(R) = h\nu$ at any internuclear separation, and the
spectrum resembles a wing to the central atomic transition.
Observation of the absorption process is made through some
direct or cascading transitions in the collision product
(see Figure 1).

   In one of the usual approaches for obtaining absorption
spectra in atom-atom collisions the beam of a tunable laser
is passed through a cell containing a metal atom - rare gas
mixture, M - RG. The absorption of a laser photon by a
M - RG pair creates a M^{*} - RG pair, which then may separate
to products, M^{*} + RG. The intensity of the M^{*} fluorescence
is proportional to the absorption coefficient $K(\lambda)$; the
typical shape of such a spectrum using photon counting tech-
niques[4] is shown in Figure 2c. The measurement then is re-
peated for various temperatures of the vapor cell; this is
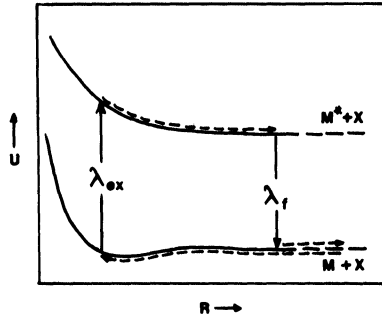
FIGURE 1   Schematics of absorption during atom-atom
            collisions.

necessary to deduce the two potentials unumbiguously, as
will be outlined below.

    For the interpretation of the observed line profiles
various models have been utilized; for example, profiles can
be described, at least partially, by the quasi-static theo-
ry.   According to this interpretation, the absorption coef-
ficient is given by

$$K(\lambda) \backsim 4\pi \cdot R^2 n_M n_{RG} \cdot f(R) \cdot \exp(-(U^*(R)-U(R))/kT) \cdot dR/d\lambda \quad (2)$$

Here n_M and n_{RG} are the concentrations of perturbed and per-
turbing atoms, $f(R)$ is the oscillator strength of the tran-
sition, T is the temperature and U^* and U are the interac-
tion potentials between the perturber and the atom in its
initial or final state, respectively.   However, when there
is an extremum in the difference between upper and lower
state potentials the spectrum generally exhibits so-called
"satellites".   In this region the quasi-static approxima-
tion is no longer valid, and a more refined interpretation
has to be used, for example, the unified Franck-Condon (UFC)
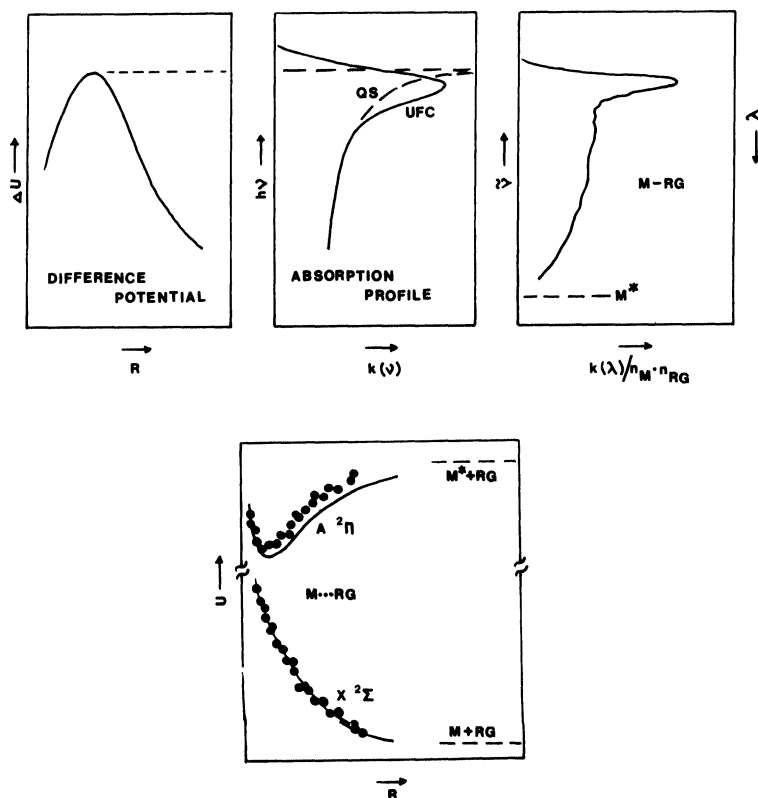treatment[5] (see Figure 2b).

FIGURE 2   Wing spectra in atom-perturber collisions;
(a) difference potential, (b) quasi-static
(QS) and unified Franck-Condon (UFC) pro-
files, (c) experimental absorption spectrum
(d) potentials deduced from spectra like in
(c).

According to relation (2), the temperature dependence
of the absorption spectrum can be interpreted as follows: at
a given λ the plot $\ln K(\lambda) = -(1/T)$ is a streight line, and
its slope yields $U(R_\lambda)$. The upper state potential, $U^*(R_\lambda)$,
is then obtained by adding the difference potential (propor-
tional to the photon energy) to this potential (see Figure

H. H. TELLE

2d). Such experimental potentials can be compared with
those from theoretical calculations (full lines in Figure
2d). Moreover, the absolute measurement of the intensity of
the absorption spectrum leads to the determination of the
oscillator strength of the transition as a function of R.

3. PRINCIPLES OF A HALF-COLLISION

3.1. Photodissociation and emission during the course of
     separation

Molecules may be dissociated by photoexcitation; if this
dissociation proceeds on a potential surface which correla-
tes to an excited product state then fluorescence from that
excited state is expected. Accompanying the strong atomic
emission for infinitely separated particles weak wings may
also be observed originating from the molecular complex in
the course of falling apart. The situation is shown sche-
matically in Figure 3; the dashed lines for the wing emis-
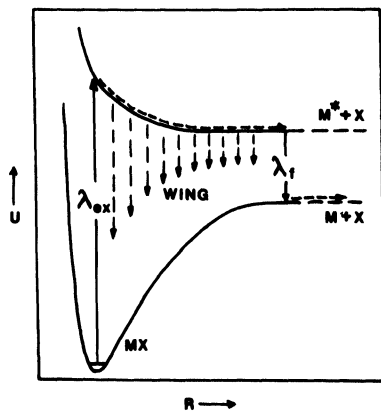sion indicate that the intensity observed is very small

FIGURE 3   Schematics of emission during dissociation
            following the excitation with a photon.

in comparison to the fluorescence at wavelength λ_f. The
spectra obtained from the emission of the transient dissoci-
ating state can be linked to the interaction potentials. In
general, this poses a simplification over the case where a
full atom-atom collision has to be considered, since initial
conditions for the photodissociation process (a half-colli-
sion) are usually quite distinct. Wing spectra originating
from the described process have been observed in the photo-
dissociation of NaI[2]. In the corresponding experiments NaI
contained in a vapor cell is dissociated by the radiation
of a KrCl laser; strong emission of the sodium D-line is ob-
served. The accompanying wings are 5 to 7 orders of magni-
tude weaker than the atomic emission but nevertheless show
interesting structure; however, interpretation of the spec-
tra in terms of molecular potentials is still not complete.

3.2. Induced absorption and emission phenomena

The experimental scheme utilized for the NaI photodissocia-
tion can be improved significantly. One major restriction
in a vapor cell experiment is the relatively high tempera-
ture needed to produce sufficient particle densities; this
in turn results in a rather broad population distribution,
and the advantage of the half-collision scheme is diminished.
The situation improves dramatically when molecular beam
techniques are applied. In a seeded beam the effective ro-
tational and vibrational temperatures can be lowered signi-
ficantly, so that only a few very low lying energetic states
are populated. One may also wish to increase the sensitivi-
ty in the detection channel. As it has been pointed out
above the spontaneous emission during the separation of the
molecule to its atomic products is very weak; the signal
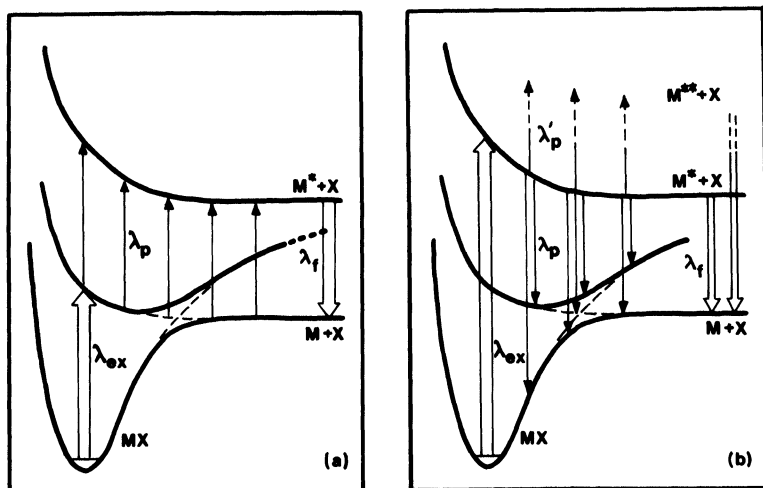strength can be largely enhanced when using laser-induced

FIGURE 4   Schematics of laser-induced processes during
            photodissociation; (a) stimulated absorption
            from a potential leading to ground state pro-
            ducts, and (b) stimulated emission from a
            potential leading to excited state products,
            where various lower potentials may be acces-
            sed; alternatively, also stimulated absorp-
            tion to higher potentials is feasible.

processes. This has the further advantage that also poten-

tials are accessible which lead to nonradiative product

states.

    In Figure 4a the schematics for induced absorption are

shown. A strong laser at wavelength λ_{ex} excites the mole-

cule to the dissociative branch of a potential correlating

to ground state products; this laser may also be tunable in

order to access various parts of the repulsive potential.

While the molecule is en route to products a second laser

probes the corresponding potential. The successful absorp-

tion of a photon can be observed via the emission from the

then excited atomic product. In this way the complete po-

tentials from the internuclear separation of dissociative
excitation out to infinite separation of the product atoms
can be explored. The procedure closely resembles the atom-
atom collision described in section 2, but only for a half-
collision.

The induced emission scheme to replace the spontaneous
emission case described above is shown in Figure 4b. The
exciting laser now transfers the molecule to a dissociative
potential correlating to excited products. The tunable
laser then induces downward transitions from the potential
on which the molecule separates to lower lying potentials;
this is indicated in the figure by multiple arrows. The
successful induced emission may be detected via a decrease
in emission intensity in the atomic product. However, this
could be rather difficult; the change in atomic emission
intensity may be minute because only rather small fractions
of all particles may suffer induced downward transitions.
To overcome this problem induced absorption to higher lying
potentials could be helpful since this creates atomic emis-
sion lines differing from the original $M^* \rightarrow M$ line; this pro-
cess is indicated by the dashed lines in Figure 4b.

4. <u>PRELIMINARY RESULTS AND DISCUSSION</u>

The procedure outlined in the previous section is now being
tested in its initial stages with NaI in order to have data
from the spontaneous emission scheme for comparison.

The experimental set-up is shown in Figure 5. Since
the processes to be observed are rather feeble sufficient
particle densities are required. This can be achieved with
a high-flow seeded beam source for molecules developed
earlier[3]. NaI densities comparable to those in a vapor cell
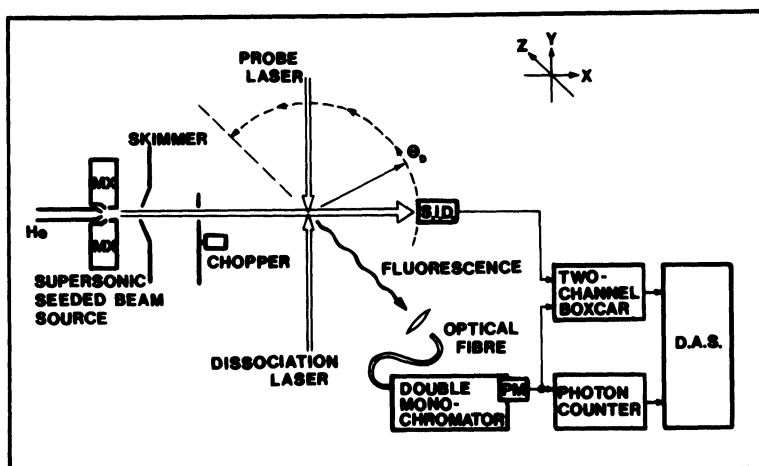can be produced. The molecular beam is irradiated perpen-

FIGURE 5   Experimental set-up.

dicular by two counter-propagating laser beams. One is the
dissociating laser at wavelength λ_{ex}, whereas the second
laser induces transitions during the separation of the mole-
cule at the tunable wavelength λ_p. Two detectors are avail-
able in the experiment. The dissociation to ground state
products may be detected by a surface ionization (S.I.) de-
tector, which can be moved around the interaction volume.
As a bonus the angular distribution of the photodissociation
products can be traced. The fluorescence signal from the
sodium D-line is filtered by a double-monochromator; in
this way straylight from the lasers and parasitic fluores-
cence can be suppressed. Alternatively the monochromator
can select short-wavelength atomic transitions when induced
absorption is used as in the case depicted in Figure 4b.
The signals from the photomultiplier and the S.I. detector
are sampled with a photon-counting / boxcar-integrator
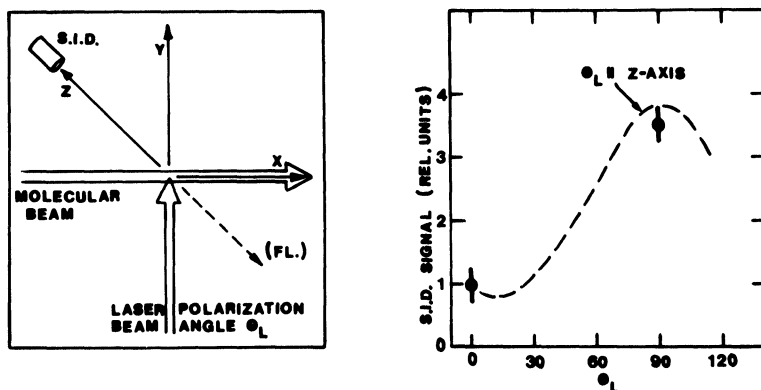arrangement and handled by a data aquisition system.

FIGURE 6   Test data; dependence of the photodissocia-
             tion probability on the polarization of the
             exciting laser.

     In a preliminary study the S.I. detector was set at 90°
to both the molecular and laser beam. In Figure 6 the mea-
sured relative intensity from the S.I. detector is plotted
as a function of the polarization of the dissociation laser,
in this study the 3rd harmonic of a Nd:YAG laser; its pola-
rization is with respect to the axis of the S.I. detector.
The results are in good agreement with other measurements[6].

     For the step of stimulated absorption the 2nd harmonic
of the same Nd:YAG laser has been used. This wavelength is
sufficiently far from the centre D-line to be outside the
Lorentz core. Strong emission of the sodium D-line is ob-
served.

     The two fixed wavelengths in these test measurements
will now be replaced by the output from two tunable dye
lasers to probe the complete range of internuclear separa-
tions.

     Measurement of the wing spectra, both for the induced
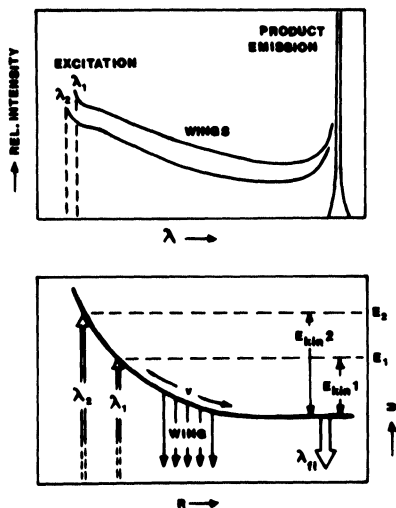absorption and/or emission, for various excitation wave-

H. H. TELLE

FIGURE 7   Conversion procedure from experimental wing
            spectra to molecular potentials, in depen-
            dence from the excitation wavelength.

lengths resembles an equivalence to the temperature depen-
dence in the absorption during atom-atom collisions. The
respective dissociation energies result in different kinetic
energies with which the atoms recess from their transient
configuration on the repulsive potential. The situation is
schematically shown in Figure 7.

    For any frequency ν_p of the probe laser the emitted
fluorescence intensity in the D-line is correlated to the
time the atoms linger at the corresponding internuclear dis-
tance,

$$I_f(\nu_p, E_i) \sim |D(R_p)|^2 \cdot v_i(R_p)^{-1}$$

$$= |D(R_p)|^2 \cdot (2(E_i - U^*(R_p))/\mu)^{-\frac{1}{2}} \quad ; \quad (3)$$

E_i stands for the dissociation energy at the i-th excitation
wavelength, $v_i(R)$ is the recoil velocity at distance R, and

μ is the reduced mass of the molecule. The intensity ratio, Q, for different energies, say E_1 and E_2 (corresponding to λ_1 and λ_2), is

$$Q = (I_f(\nu_p, E_1)/I_f(\nu_p, E_2))^{\frac{1}{2}}$$

$$= (E_1 - U^*(R_p)) \, / \, (E_2 - U^*(R_p)) \qquad , \qquad (4)$$

and one deduces for the potential of the excited state

$$U^*(R_p) = (E_1 - Q \cdot E_2) \, / \, (1-Q) \qquad , \qquad (5)$$

while the difference potential ΔU is related to the transition frequency ν_p by $h\nu_p = \Delta U(R_p) = U^*(R_p) - U(R_p)$. Hence, both potentials can be derived from the wing spectra. The well known position of the minimum of the ground state, from which the dissociation step starts, serves as a reference point in the scale of internuclear separations. Care should be taken that the fluorescence intensity in the product state follows the strength of the probe laser radiation linearly, otherwise a conversion from the observed spectra to molecular potentials is not possible.

5. CONCLUSION

We have shown that the proposed scheme of induced absorption and emission for the investigation of molecules in the process of falling apart is feasible. The procedure will be of superior sensitivity to the previously used method of wings produced by spontaneous emission, and a precise tracking of repulsive potentials should now be possible.

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