ROTATIONALLY INELASTIC SCATTERING OF FORMALDEHYDE

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State to state rotationally inelastic and elastic
differential cross-sections for the system D_2CO-H_2
have been measured at a center of mass energy of 17 meV
A single rotational state of D_2CO (1_{10}) of high state
purity is focused into the scattering region by com-
bining rotational cooling and electric state selection.
The final rotational state is probed angle dependent
by LIF using a frequency doubled CW ring dye laser
at 325 nm. The full range of CM angles is probed.
We present the first results of the $1_{10} \rightarrow 1_{11}$ inelastic
scattering.

1. <u>INTRODUCTION</u>

Rotationally inelastic scattering of formaldehyde from
H_2 is of interest as collisional cooling seems the most
probable mechanism to explain the observed anomalous absorp-
tion of interstellar formaldehyde. To test interstellar
models either absolute state to state excitation cross-
sections at interstellar conditions or a reliable intermole-
cular potential are needed. The problem has been attacked
experimentally by a variety of techniques:
    - Cell experiments[1]: such as MW line broadening, MW
steady state double resonance and time resolved double
resonance. These experiments give physical quantities

related to integral cross-sections, however mostly at room-
temperature conditions with a wide velocity distribution
and many rotational states populated. The effects are the
result of all possible inelastic collisions, elastic effects
and wall collisions.

    - Beam experiments using electrostatic state selection
and a scattering cell[2]: such as Maser type and EBR type with
double resonance. In these experiments one can induce single
collisions, however one is limited to small scattering
angles which implies that only for large interactions (e.g.
dipole-dipole) a considerable fraction of the integral
cross-section can be measured. Also the relative velocity
is still high compared to interstellar conditions.

    We present the first results of a crossed beam experi-
ment with laser induced fluorescence (LIF) detection. The
isotope D_2CO is used instead of H_2CO as its fluorescence
yield is about 100 times larger. Both initial and final rota-
tional state are well defined. The differential cross-section
is measured over the entire center of mass (CM) angular
range.

2. EXPERIMENT

    A CW formaldehyde beam is produced by heating paraform-
aldehyde to $100^\circ C$ in an oven producing about 150 Torr vapour
pressure. Up to 1200 Torr argon is added as carrier gas and
the mixture is expanded through a 50 μm nozzle. The beam is
formed by a 1 mm skimmer.

    The D_2CO beam is detected by LIF with a UV laser. The UV
laser beam is produced by frequency doubling in a $LiIO_3$ crys-
tal inside the cavity of a single frequency CW ring dye
laser[3]. Tuning is possible over a wavelength region of

295–334 nm with typically 2 mW output power. The laser line-
width is about 0.5 MHz. The D_2CO spectrum is spectroscopical-
ly well established[4]. The transition $X^1A_1(v=0) \rightarrow A^1A_2(v_2=2,$
$v_4=1)$ at 325 nm is probed which is the strongest band within
the laser range. The transition is not saturated. The lower
rotational states of ortho-D_2CO (1_{11}, 1_{10}, 2_{12}, etc.) are
probed in the $^RR_1(J)$ branch. From the relative intensities a
rotational temperature of 6 K is determined.

To prepare a single rotational state a quadrupolar elec-
trostatic state selector is used which focuses molecules in
a state with positive Stark effect onto the machine axis. In
the polar D_2CO (2.34 D) the Stark effect is very strong for
the closely spaced K-doublet states with low J value. The 1_{10}
state is focused most efficiently; a population enhancement
of a factor of 20 in the scattering region can be achieved,
yielding a signal to noise ratio of 5000 at RC=1s. At 10 kV
the 1_{10} and 1_{11} ortho D_2CO states are populated for 92% and
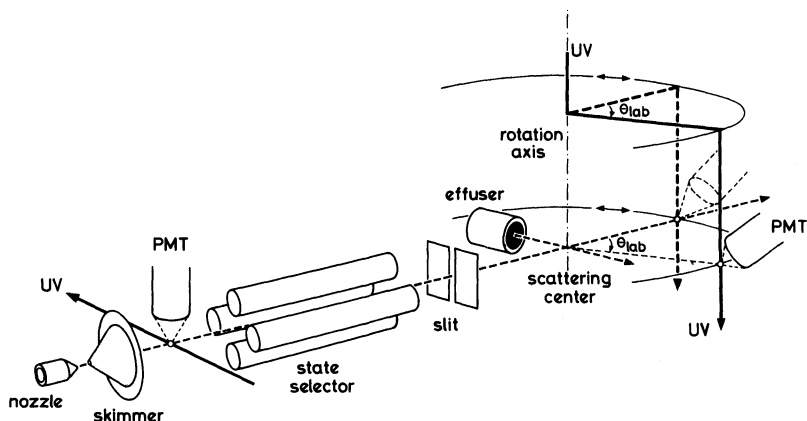2% respectively.

FIGURE 1   Schematic experimental set-up.

The lines detected have a linewidth of 6.5 MHz caused by
residual Doppler broadening by molecular beam and laser beam
divergence. The narrow linewidth makes it necessary to lock
the laser to the molecular transition. This is done by
coupling a small fraction of the laser beam into a second
LIF detection system between skimmer and state selector;
this fluorescence signal is fed back to the laser to stabi-
lize the frequency within 1 MHz. Stabilization in front of
the state selector enables also to lock on states which are
defocused by the state selector and thus hardly present in
the scattering region.

The D_2CO beam enters the scattering region via a slit
1 mm wide, after which it is crossed with a thermal effusive
H_2 beam at 77 K. As the effuser geometry is known and the H_2
flow is controlled within 2% and calibrated the absolute H_2
density distribution is known. The D_2CO beam velocity is
760 m/s with a width $\Delta v/v$ of 0.10. The H_2 beam has a most
probable velocity of 1060 m/s. So the center of mass trans-
lational energy is 17 meV (195 K).

Although the use of optical fibers is a practical solu-
tion in angle dependent measurements[5], our system is desig-
ned without fibers as they introduce a relatively high loss
of laser power in the UV region compared to well coated
mirrors. The UV laser is focused within 1 mm at 83 mm from
the scattering center, so the angular resolution is 0.7° in
the lab. system. The fluorescence radiation is collected in
the focus of a paraboloid mirror with an efficiency of about
70% of the entire solid angle. As most of the fluorescence
radiation is at a wavelength above 350 nm cut-off filters are
used to reduce the resonant background from scattered laser
light. The fluorescence detection system and the windows and
mirrors for the laser beam are mounted on a rotatable flange

with the rotation axis through the scattering centre. The
laser is directed along the rotation axis which enables
probing around the scattering centre by simply rotating the
flange without further adjustment of the laser beam
(figure 1).

A computer controls the flange rotation, switching on
and off of the H_2 beam and the data acquisition. Measurements
of the angle dependent signal with the secondary beam and
laser beam on and off are performed in an inversion symme-
tric measuring cycle including the signal in forward direc-
tion. In this way linear drift if present is corrected for,
and all angle dependent intensities are measured relative
to the forward unattenuated signal.

3. EXPERIMENTAL RESULTS AND INTERPRETATION

Figure 2 shows the angle dependence of the signal
intensity at the J=1 K-doublet states (1_{10}, 1_{11}) relative to
the unattenuated signal ($I(\vartheta)/I^0$) at 10 kV state selector
voltage and a fixed H_2 flow. The dashed line shows the
angular dependence of the unattenuated beam; the width is
geometrically determined by the entrance slit of the scat-
tering region and the laser focus. Only for laboratory angles
beyond $1.5°$ one can be sure to measure only signal from
scattered molecules.

To relate these curves to a differential cross-section
$\frac{d\sigma}{d\Omega}(\vartheta,\phi)$ the general definition is recalled:

$$\frac{dN}{d\Omega}(\vartheta,\phi) = n_1 n_2 v_r \Delta V \frac{d\sigma}{d\Omega}(\vartheta,\phi)$$

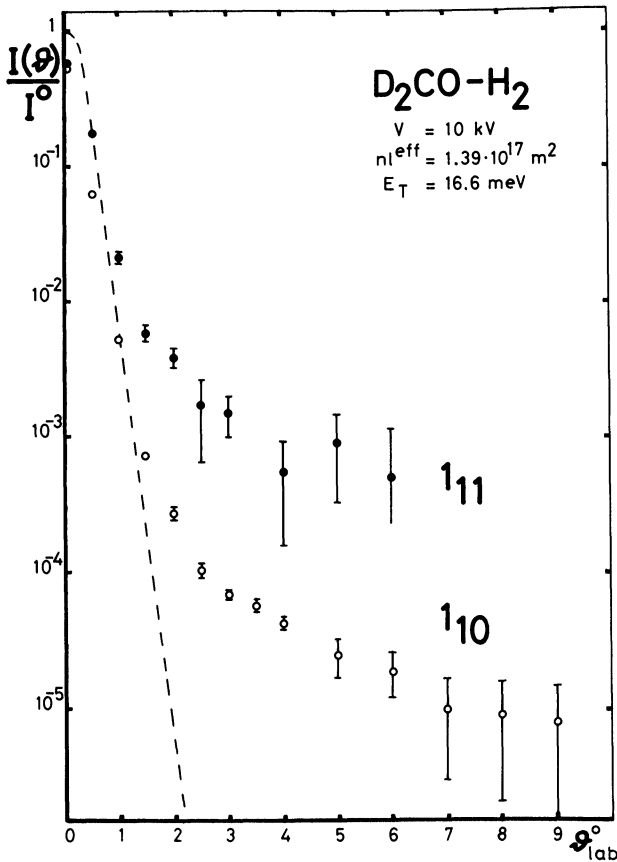with $\frac{dN}{d\Omega}(\vartheta,\phi)$ the flux of scattered molecules into a solid

FIGURE 2   Signal intensity versus ϑ_{lab} for the 1_{10} and 1_{11}
            states.

angle $d\Omega$ in direction (ϑ, ϕ); n_1 and n_2 are the density of
primary and secondary beam molecules in the scattering volume
ΔV; v_1 and v_r are the primary beam velocity and relative
velocity, respectively. As in the experiment the secondary
beam density has a distribution $n_2(z)$ along the primary beam
direction z it is convenient to define the effective nl
product:

$$nl^{eff} = v_r/v_1 \int_{-\infty}^{\infty} n_2(z) z \, dz$$

If one observes collision induced transitions of the primary molecules into a state $|i>$ within a solid laboratory angle $\Delta\Omega(\vartheta)$ in the scattering plane one can write:

$$N_i(\vartheta) = nl^{eff} \sum_j d\sigma_{ji}(\vartheta) N_j^0$$

with N_j^0 the unattenuated beam flux in state $|j>$ and $d\sigma_{ji}(\vartheta)$ the state to state $(|j> \to |i>)$ differential cross-section integrated over $\Delta\Omega(\vartheta)$. The observed signal intensity is via
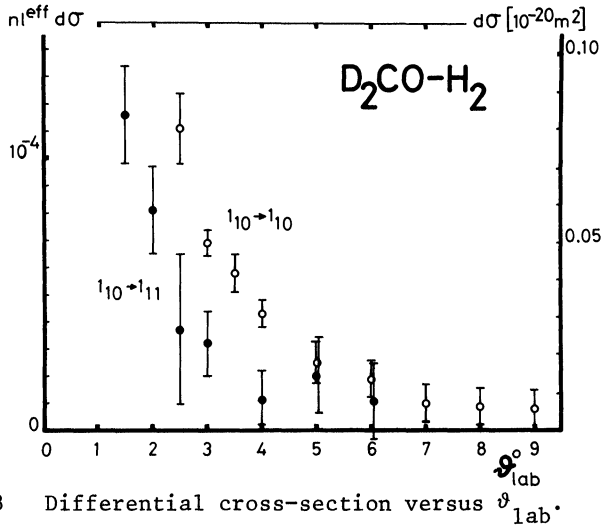

FIGURE 3   Differential cross-section versus ϑ_{lab}.

the line strength directly proportional to the molecular flux in the probed state. In our state selected beam one initial state, 1_{10}, is predominantly present, thus one expects:

$$I_i(\vartheta)/I_i^0 = nl^{eff} \, d\sigma(1_{10} \to i)(\vartheta) \, N^0(1_{10})/N_i^0$$

From the observed line intensities it is known that

$N^0(1_{10})/N^0(1_{11})$ has the value 46(2). Figure 3 shows $nl^{eff}d\sigma$
for $1_{10} \rightarrow 1_{10}$ and $1_{10} \rightarrow 1_{11}$ versus ϑ_{lab}. In order to compare
these experimental results with theoretical predictions it
is necessary to transform the results to the CM frame   As
the heavy scattering partner D_2CO is detected the range of
laboratory scattering angles is kinematically restricted to
$\vartheta_{lab} < 13°$. Within this range both forward and backward CM
scattering are detected at the same ϑ_{lab}. The transformation
from lab to CM frame and vice versa is given through a func-
tion $F(\vartheta_{lab}, \vartheta_{cm})$ which is calculated by a Monte Carlo simula-
tion taking into account the density and velocity distribu-
tion of the secondary beam and the finite resolution of the
detector ($\Delta\vartheta_{lab} = 0.7°$, effective height $h = 3$ mm). $F(\vartheta_{lab}, \vartheta_{cm})$
is normalized such that

$$\Delta\Omega_{cm} = \int_0^\pi d\vartheta_{cm} \, 2\pi \sin\vartheta_{cm} \, F(\vartheta_{lab}, \vartheta_{cm})$$

and thus

$$d\sigma(\vartheta_{lab}) = \int_0^\pi d\vartheta_{cm} \, 2\pi \sin\vartheta_{cm} \, F(\vartheta_{lab}, \vartheta_{cm}) \frac{d\sigma}{d\Omega}(\vartheta_{cm})$$

Figure 4 shows $F(\vartheta_{lab}, \vartheta_{cm})$ for $\vartheta_{lab} = 2°$. Clearly the kinema-
tics are quite unfavourable as the CM resolution is about
$20°$ for the forward scattering. The same calculation also
yields $nl^{eff} = 1.39 \ 10^{17} \ m^{-2}$ for the fixed H_2 flow in the ex-
periment. This enables us to assign absolute values to the
data points in figure 3.

    In principle the measured cross-sections can be deconvo-
luted to absolute differential CM cross-sections however
the limited number of data points and the present CM
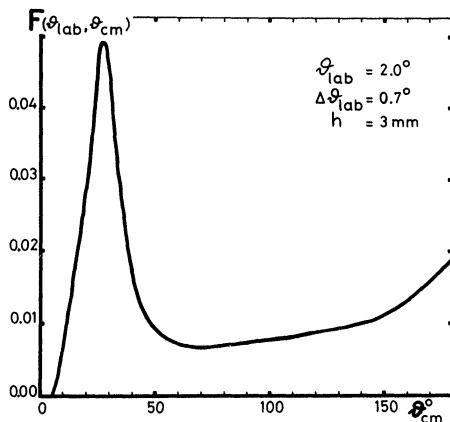angular resolution do not justify such an effort at this
stage of the experiment.

FIGURE 4   Apparatus function for $\vartheta_{lab} = 2°$.

Quantitatively it is observed that the elastic $(1_{10} \rightarrow 1_{10})$ and inelastic $(1_{10} \rightarrow 1_{11})$ cross-sections peak strongly in forward direction probably due to dipole-quadrupole interaction. For small angles the elastic cross-section is about 3 times the inelastic cross-section. At larger angles where the repulsive potential is probed both cross-sections tend to the same value.

4. CONCLUSIONS

Although the results are still preliminary this experiment demonstrates clearly the strength of the combination of state selection and laser induced fluorescence in determining inelastic state-to-state differential cross-sections.

Further improvement of the angular resolution, introduction of a secondary nozzle beam and enhancement of the SNR will lead to more quantitative results in the CM system.

Measurements of transitions with $\Delta J > 0$ by probing higher rotational states are in progress.

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