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WINTER COLLEGE ON

ATOMIC AND MOLECULAR PHYSICS

(9 March - 3 April 1987)

SYMMETRY PROPERTIES OF MOLECULAR ENERGY LEVELS
SPECTROSCOPY OF IONS AND FREE RADICALS

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SYMMETRY PROPERTIES OF MOLECULAR ENERGY LEVELS

PRIMARY CONCERN: INVARIANCE OF THE HAMILTONIAN
TWO APPROACHES, VIA TRANSFORMATION PROPERTIES (1) OF THE HAMILTONIAN UNDER PERMUTATIONS OF IDENTICAL PARTICLES + INVERSION (PI-GROUPS), (2) OF THE NUCLEI AND THEIR DISPLACEMENTS (POINT GROUPS)

GROUP: SET OF ELEMENTS (OPERATIONS, OPERATORS, ..) WHICH SATISFY CERTAIN COMBINATION RULES

SYMMETRY OPERATIONS:

- PI GROUPS: PERMUTATIONS + INVERSION
- POINT GROUPS: BF INVERSION $\hat{=}$ (POINT), PROPER C_n AND IMPROPER S_n ROTATIONS (LINE; n MEANS ROTATION OVER $2\pi/n$) AND REFLECTIONS σ_v, σ_h, σ_d (PLANE)
  - σ_v PLANE CONTAINS C_n AXIS
  - σ_h PERPENDICULAR TO C_n AXIS
  - σ_d BISECTING PLANE

REPRESENTATION: A SET OF MATRICES REPRESENTING THE EFFECT OF THE GROUP OPERATIONS ON A SET OF VECTORS, FUNCTIONS, ... BASIS SQUARE $n \times n$ MATRICES (n = DIMENSION OF THE REPRESENTATION), THEIR PRODUCTS MUST FOLLOW COMBINATION RULES OF THE GROUP; THE SAME DIMENSION FOR ALL ELEMENTS OF THE GROUP.

IRREDUCIBLE REPRESENTATION: A SET OF SQUAR MATRICES OF SMALLEST POSSIBLE DIMENSION ($n = 1, 2, 3, \ldots$) WHICH FORM A REPRESENTATION OF THE GROUP; THIS DIMENSION CANNOT BE REDUCED BY ANY TRANSFORMATION

GROUP NOMENCLATURE

C_n ROTATIONAL SYMMETRY FOR ROTATION OVER AN ANGLE $2\pi/n$

D_n AS ABOVE, BUT THERE ARE ALSO n C_2 AXES PERPENDICULAR TO C_n

SUFFIX v THERE IS A (NORMALLY n) σ_v PLANE
h THERE IS A HORIZONTAL SYMMETRY PLANE

EX. C_{2v}, C_{3v}, D_{2h}, ..., $C_{\infty v}$, $D_{\infty h}$

CUBIC GROUPS HAVE SPECIAL SYMBOLS:
T_d = TETRAHEDRAL .. O_h = OCTAHEDRAL

NOMENCLATURE IR-REPRESENTATIONS *)

1-DIM.	A - SYM B - ANTISYM.	) FOR C_n
SUBSCRIPT	1 - SYM. 2 - ANTISYM	) FOR σ_v OR C_2
PRIME	′ - SYM. ″ - ANTISYM.	) FOR σ_h OR S_n

Σ

*) DETERMINED BY THE PROPERTY OF THE TRACE OF THE REPRES. MATRICES

T, A, .. 2 DIMENS. .. E
3 DIMENS .. F
(SUBSCRIPTS & PRIMES AS ABOVE: $E_1, F_2, E', \ldots, F_1, F_2$.)

→ FUNDAMENTAL RULE : DIM. OF A REPRESENTATION EQUALS (ESS.) DEGENERACY OF THE Q.M. EIGENVALUE (S).

A, B - NON DEGENERATE
E - DOUBLY DEGENERATE
F - TRIPLY DEGENERATE

GROUPS: C_{2v}, C_{2h} ..... ONLY 1-DIM. REPRES.
$C_{3v}, C_{3h}, \ldots, C_{\infty v}$ 1 & 2 DIM. REPR.
D_{2h}, D_{2d} ..... ONLY 1-DIM. REPR.
$D_{3h}, D_{3d}, \ldots, D_{\infty h}$ 1 & 2 DIM. REPR.
T_d, O_h 1, 2, 3 DIM. REPR.

EX. OF GROUPS & IR

C_{2v} (H_2O) SYM. OPERATIONS $E, C_2, \sigma_v, \sigma_v'$ ($E = A$)
SPECIES A_1, A_2, B_1, B_2

C_{3v} (NH_3) SYM. OPERATIONS $E, 2C_3, 3\sigma_v$
SPECIES A_1, A_2, E ($E = A$)

$C_{\infty v}$ (OH) SYM. OPERATIONS E, C_φ, σ_v
SPECIES $\Sigma^+, \Sigma^-, \Pi, \Delta, \ldots$ ($\Sigma = A$)
$A_1, A_2, B_1, E_1, \ldots$

D_{2h} SYM. OPERATIONS $E, C_2^{x,y,z}, i, \sigma(xy), \sigma(xz), \sigma(yz)$ ($E = A$)
SPECIES $A_g, B_{1g}, B_{2g}, B_{3g}, \ldots$

*) VALUES OF THE PRESCRIBED TRACES (= CHARACTERS) WHICH CHARACTERIZE IRRED. REPRESENTATIONS CAN BE FOUND IN MANY BOOKS

D_{3h} (BH_3) SYM. OPERATIONS $E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v$
SPECIES $A_1', A_2', E', A_1'', A_2'', E''$
($z = A_2''$)

$D_{\infty h}$ (H_2) SYM. OPERATIONS $E, C_\varphi, \sigma_v, i$ ($z = \Sigma_u^+$)
SPECIES $\Sigma_{g,u}^+, \Sigma_{g,u}^-, \Pi_{g,u}, \Delta_{g,u}, \ldots$

T_d (CH_4) SYM. OPERATIONS $E, 8C_3, 3C_2, 6S_4, 6\sigma_d$
SPECIES A_1, A_2, E, F_1, F_2

CONVENTION: WHEN MOLECULAR CONFIGURATION AND/OR MOLECULAR HAMILTONIAN HAS SYMMETRY OF A CERTAIN GROUP IR. REPRESENTATIONS ($A_1, A_2, B_1, E, F_1, F_2, \ldots$) ARE USED TO ORDER MOLECULAR STATES.

GENERALLY TRANSITION IS ALLOWED WHEN

$$\langle f | \underline{A} | i \rangle \subset A_1$$

i.e. IS INVARIANT UNDER ALL SYMMETRY OPERATIONS OF THE MOLECULAR SYM. GROUP, i.e. WHEN THE PRODUCT OF THE SYMMETRIES OF $|f\rangle$ AND $|i\rangle$ HAS THE SYMMETRY OF $\underline{A}$ = $\underline{\mu}_e$ (E1), $\underline{\mu}_m$ (M1), $\underline{Q}$ (E2), $\underline{\underline{\Theta}}, \ldots$

EXPERIMENTS ARE PERFORMED IN A LABORATORY (SPACE) FIXED (SF) FRAME. FUNDAMENTAL SYMMETRY OPERATIONS IN THIS FRAME ARE:

SF INVERSION ($\underline{I}$) → PARITY $\underline{I}\Psi = \pm\Psi$

PERMUTATION ($\underline{P}$) OF IDENTICAL NUCLEI (& ELECTRONS)

$$\underline{P}\Psi = \begin{cases} +\Psi & \text{FOR BOSE-EINSTEIN} \\ -\Psi & \text{FERMI-DIRAC STAT.} \end{cases}$$

DIATOMICS

IF COUPLING BETWEEN ELECTRONIC (ψ_e), VIBRATIONAL (ψ_v), ROTATIONAL (ψ_r) AND NUCLEAR WAVEFUNCTIONS (MOTIONS) ABSENT OR WEAK THE MOL. WAVE-FUNCTION CAN BE WRITTEN AS:

$$\psi = \psi_e \psi_v \psi_r \psi_I$$

$$\underline{I}\psi = \begin{cases} +\psi & \text{POSITIVE} \\ -\psi & \text{NEGATIVE} \end{cases} \text{ STATES}$$

THIS APPLIES TO ALL DIATONIC MOLECULES:

$$\underline{P}\psi = \begin{cases} +\psi & \text{SYMMETRIC (s)} \\ -\psi & \text{ANTISYMMETRIC (a)} \end{cases} \text{ STATES}.$$

SELECTION RULES:

	E1	M1	E2	...
PARITY CHANGE	YES	NO	NO	...

EXCHANGE ($\underline{P}$) $\quad s \leftrightarrow s,\ a \leftrightarrow a,\ s \not\leftrightarrow a$

(CONSERVATION OF THE NUCLEAR SPIN SYM.)

ELECTRONIC ORBITAL STATES

SYM. OPERATIONS: $C_\infty(z), \sigma_v, \underline{i}$ (HOMONUCLEAR)

$C_\varepsilon(z)$ MATRIX REPRESENTATION

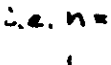
$$C_\varepsilon(z) = \begin{pmatrix} \cos n\alpha & -\sin n\alpha \\ \sin n\alpha & \cos n\alpha \end{pmatrix} \qquad \varepsilon = n\alpha$$

NON-DEGENERATE REPR. (STATES)

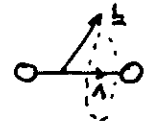
(Ξ) INVARIANT UNDER C_ε → TRANSFORM WITH $n = 0 \rightarrow \Sigma$ STATES

DOUBLY DEGENERATE REPR. (STATES): THE TWO STATES TRANSFORM AS

1. $\alpha \rightarrow \Pi$
2. $\alpha \rightarrow \Delta$
3. $\alpha \rightarrow \Phi$ ETC.



i.e. $n = \Lambda = \pm 1, \pm 2$



ENERGY DEPENDS ONLY ON Λ^2, HENCE THE DOUBLE DEGENERACY (Λ-DEGENERACY)

C_ε LABEL NOT SUFFICIENT TO SPECIFY THE STATE COMPLETELY

σ_v

$$\sigma_v^2 = 1 \rightarrow \sigma_v \psi_e = \pm \psi_e \rightarrow \Sigma^+, \Sigma^-,$$

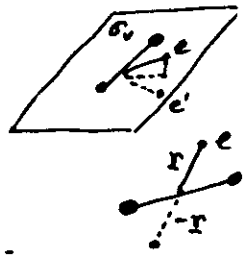
↳ PARITY OF THE ORBITAL EL. STATE

NOT FOR DEGENERATE STATES

$\underline{i}$

$$\underline{i}^2 = 1 \rightarrow \underline{i}\psi_e = \pm \psi_e$$

$+$ = GERADE
$-$ = UNGERADE



FOR ALL STATES: $\Sigma^\pm_{g,u}, \Pi_{g,u}, \ldots$

PARITY: CAN BE WORKED OUT ASS. ψ_I HAS A DEFINIT. (+) PARITY AND USING THE EQUIVALENCE

$$\underline{I} \equiv \sigma_v$$

$$I\psi = (I\psi_e)(I\psi_v)(I\psi_r)$$
$$= (\sigma_v \psi_e)(+\psi_v)((-)^J \psi_r) \text{ ETC.}$$

EXCHANGE: USE THE EQUIVALENCE

$$\underline{P} \equiv \underline{I} \cdot \underline{i} = \sigma_v \cdot \underline{i}$$

$$P\Psi = \underbrace{\left(\pm\right)\left(\begin{matrix}g\\u\end{matrix}\right)}_{\Psi_e}\underbrace{(+)}_{\Psi_v}\underbrace{(-)^J}_{\Psi_r}\underbrace{\left(\begin{matrix}+\\-\end{matrix}\right)}_{\Psi_I} = \begin{cases}+ & \text{FOR BE}\\ - & \text{FOR FD}\end{cases}$$

$$\begin{cases}+ & \text{FOR ORTHO}\\ - & \text{FOR PARA}\end{cases}$$

ORTHO : $I_1 + I_2 = 1$

PARA : $I_1 + I_2 = 0$

EX. H_2, Σ_g^+, $I = 1/2$ THREE NUCL. SPIN STATES

FOR ORTHO H_2: $\uparrow\uparrow, \downarrow\downarrow, \uparrow\downarrow + \downarrow\uparrow$ SYM. (+)

ONE STATE FOR PARA $\uparrow\downarrow - \downarrow\uparrow$ ANTISYM. (-)

$$(g)(+)(+)(-)^J\left(\begin{matrix}+\\-\end{matrix}\right) = (-) \quad \begin{cases}\text{ORTHO} & J = 1,3,5,..\\ \text{PARA} & J = 0,2,4,..\end{cases}$$

INTENSITY RATIO $R = \dfrac{g(\text{ORTHO})}{g(\text{PARA})} = \dfrac{3}{1}$

O_2, Σ_g^-, $I = 0$ (BE)

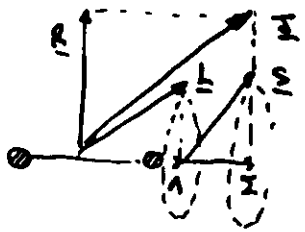
$$(g)(-)(+)(-)^J\left(\begin{matrix}+\\-\end{matrix}\right) = (+) \rightarrow J = 1,3,5,..$$

(Ψ_I (+) FOR $I_2 = 0$) LINES MISSING

ELECTRONIC SPIN

HUND'S COUPLING CASES

(a) $\underline{L}\cdot\underline{S} \ll \underline{L}\cdot\underline{A}, \underline{S}\cdot\underline{A}$



CONSERVED:

$J, \Lambda, \Sigma(S); \Omega = |\Lambda + \Sigma|$

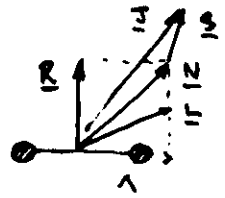
$\begin{cases} L\ S, \ldots, -S \\ L, \ldots, -L \end{cases}$

STATES: $^{2S+1}\Lambda_\Omega$

EX. $^2\Pi_{1/2,3/2}$

ANALOGOUS TO RUSSEL-SAUNDERS COUPLING

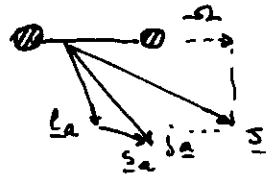
(b) $\underline{S}$ DECOUPLED FROM $\underline{A}$



$\underline{N} = \underline{R} + \underline{\Lambda}$ .. $\underline{J} = \underline{N} + \underline{S} \rightarrow J = N+S, \ldots, |N-S|$

CONSERVED: J, Λ; N ASSUMED (IF N·S COUPLING WEAK)

(c) $\underline{L}$ & $\underline{S}$ DECOUPLED FROM $\underline{A}$



CONSERVED J, Ω → $^{2S+1}\Omega^\pm$

‖ THESE ARE LIMITING CASES - REAL MOLECULES ARE ALL INTERMEDIATE

SPIN-ORBIT $\mathcal{H}_{SO} = \sum_{i,\alpha} \gamma_i(r_i)\, \underline{l}_{i\alpha}\cdot\underline{s}_i$

$\Rightarrow A\,\underline{L}\cdot\underline{S} \Rightarrow A\Lambda\Sigma$

PRODUCES MULTIPLETS; EX. $^2\Pi_{1/2}$, $^2\Pi_{3/2}$

INDICATED BY Ω

$A > 0$ NORMAL

$A < 0$ INVERTED $\Big\rangle$ FINE STRUCTURE $\left\langle \begin{matrix}\Pi_{1/2}\\ \Pi_{3/2}\end{matrix} \right\rangle$ LOWER

SPECTRUM CONSISTS OF SEPERATE Ω LADDERS OF LEVELS; TRANSITIONS BETWEEN MULTIPLETS (LADDERS) POSSIBLE IF $\Delta\Omega = \pm 1$ VALID

SPIN-ROTATION $\mathcal{H}_{SR} = \gamma\,\underline{N}\cdot\underline{S}$

IMPORTANT IN $^2\Sigma$, $^3\Sigma$, .. STATES (PRESENT ALSO IN Π, ..)

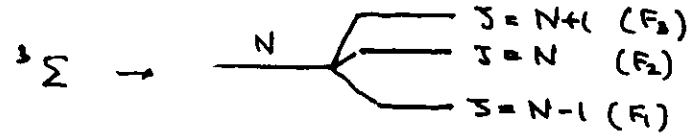
$\underline{J} = \underline{N} + \underline{S} \rightarrow \underline{N}\cdot\underline{S} = \frac{1}{2}(\underline{J}^2 - \underline{N}^2 - \underline{S}^2)$

$\Rightarrow \frac{1}{2}[J(J+1) - N(N+1) - S(S+1)]$

ALL LEVELS SPLI INTO $2S+1$ SUBLEVELS

$^2\Sigma \rightarrow$ N $\quad J = N + 1/2$ (F_2)

$\quad\quad\quad\quad\quad\quad\quad\quad J = N - 1/2$ (F_1)



ς - DOUBLING, TRIPLING, ...

O_2 .. $\gamma = -252.7$ MHz

SPIN-SPIN ($^3\Sigma$, ...)

$$\mathcal{H}_{SS}(:) \; r_{ij}^{-5}\left[(\underline{S}_i\cdot\underline{S}_j)r_{ij}^2 - 3(\underline{r}_{ij}\cdot\underline{S}_i)(\underline{r}_{ij}\cdot\underline{S}_j)\right]$$

$$\Rightarrow \lambda(3S_z^2 - \underline{S}^2)$$

O_2 .. $\lambda = 39\,667$ MHz

Λ-DOUBLING ($\Pi, \Delta, \ldots$)

$$\mathcal{H} = B\underline{R}^2 + A\underline{L}\cdot\underline{S} \quad .. \quad \underline{R} = \underline{J} - \underline{L} - \underline{S}$$

SPLITTING OF ROTATIONAL LEVELS (INTO DOUBLETS OF OPPOSITE PARITIES); REMOVAL OF THE Λ-DEGENERACY OF ELECTRONIC STATES WITH $\Lambda \neq 0$

ORIGIN: • INTERACTION OF ELECTRONIC MOTION AND ROTATION (BREAKDOWN BO-APPROX.)

• MIXING OF STATES ($^1\Pi \cdot {}^1\Sigma$, $^1\Pi \cdot {}^1\Delta$, ..)

SPLITTINGS:

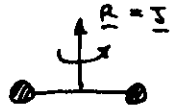
$^1\Pi$		$q\,J(J+1)$
$^2\Pi$	case (b)	$q\,N(N+1)$
$^2\Pi_{1/2}$	(a)	$a(J+1/2)$
$^2\Pi_{3/2}$	(a)	$b(J-\frac{1}{2})(J+1/2)(J+3/2)$
$^3\Pi$	(b)	$q\,N(N+1)$

≡ X. OH

VIBRATION NOT EXCITING

ROTATION A LITTLE

NO $\underline{L},\underline{S}$



$|JM\rangle = Y_{JM}(\Omega)$

$\underline{L},\underline{S} \neq 0$

MOL. BEHAVES LIKE A SYMMETRIC TOP WITH $K = \Omega$

$|J\Omega, M\rangle = D^J_{M\Omega}(\alpha\beta\gamma)$

SELECTION RULES (FOR ψ_e, ψ_v, ψ_r)

→ HYPERFINE STRUCTURE

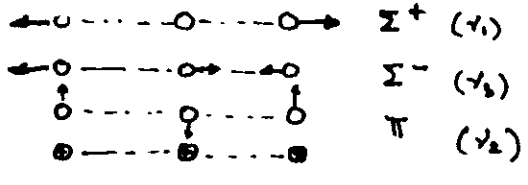
TRIATOMICS

(1) LINEAR (HCO^+, N_2H^+, ...)

GROUPS: $C_{\infty v}$, $D_{\infty h}$

VIBR. ELECTRONIC SPECIES: $\Sigma^\pm$, Π, Δ, (gu. g,u)

VIBRATIONS ($3N-5=4$)



STATES $|v_1 v_2^l v_3\rangle$

COMBINATION OF TWO $\perp$ VIBRATION (LET SAY 90° OUT OF PHASE) CAN BE SEEN AS A VIBRATIONAL ANGULAR MOMENTUM; ITS MAGNITUDE

$l\hbar$ ... $l = v_2, v_2-2, \ldots, 0$ OR 1

ENERGY DEPENDS ONLY ON l^2 → l-DEGENERACY

ELECTRONIC STATES

AS LONG AS THE MOLECULE REMAINS LINEAR

(ν_1, ν_3 VIBRATIONS) OR THE ELECTRONIC STATE IS NON-DEGENERATE SITUATION IS THE SAME AS IN DIATOMIC MOLECULES. QUITE DIFFERENT IN DEGENERATE ELECTRONIC STATES WHEN THE ν_2 (BENDING) VIBRATION IS EXCITED

RENNER-TELLER EFFECT

DURING THIS VIBRATION e.g. $D_{\infty h}$ (LIN.) SYMMETRY IS LOWERED TO C_{2v} IN WHICH THERE ARE NO DEGENERATE ELECTRONIC STATES SO THERE WILL BE SPLITTING OF VIBR. LEVELS IN DEG. ELECTRONIC STATES INTO PAIRS OF SPECIES A_1, A_2, B_1, B_2 OF C_{2v}

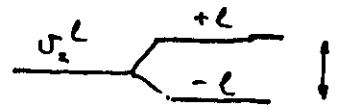
REASON:

ELECTRONIC POT. (SOLUTION OF THE ELETRONIC WAVE EQUATION) IS DIFFERENT IN THE LINEAR AND IN THE BENT CONFIGURATION

PRIMARILY DUE TO THE DIPOLE MOMENT (μ) INDUCED BY THE BENDING

GENERAL RULE: ESS. DEGENERACY IS TOTALLY OR PARTLY REMOVED WHEN THE SYMMETRY IS LOWERED; ONLY PERTURBATION OF SYM. METRY LOWER THAN THE "ORIGINAL" ONE CAN SPLIT DEGENERATE LEVELS.

ℓ-DOUBLING



REMOVAL OF ℓ-DEGENERACY BY THE VIBRATION-ROTATION (CORIOLIS-TYPE) INTERACTION

$$\mathcal{H}_c (:) \vec{J} \cdot \vec{p}$$

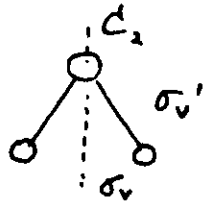
$$\Delta E = q J(J+1)$$

ℓ-DEGENERACY CAN ALSO BE REMOVED BY ℓ-TYPE RESONANCES (INTERACTION BETWEEN DEG. AND NON-DEG. VIBRATIONAL MODES DUCED BY z-ROTATION)

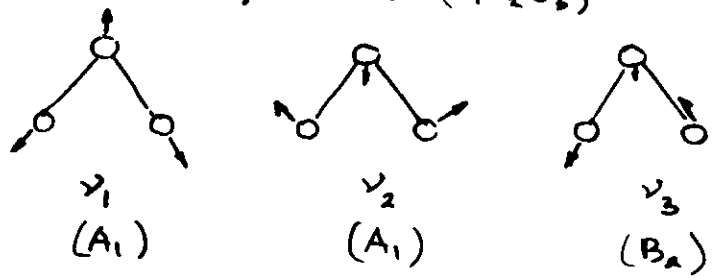
BENT CONFIGURATION ($NH_2, CH_2, \ldots, H_2O$)

NOTE: MOLECULE CAN BE BENT IN ONE (e.g. GROUND) AND LINEAR IN ANOTHER (e.g. EXCITED) ELECTRONIC (OR EVEN VIBR.) STATE.

SYMMETRY: C_{2v}; ^2A STATES: A_1, A_2, B_1, B_2 (WITH MULTIPLICITIES)



VIBRATIONS; LEVELS $(v_1 v_2 v_3)$



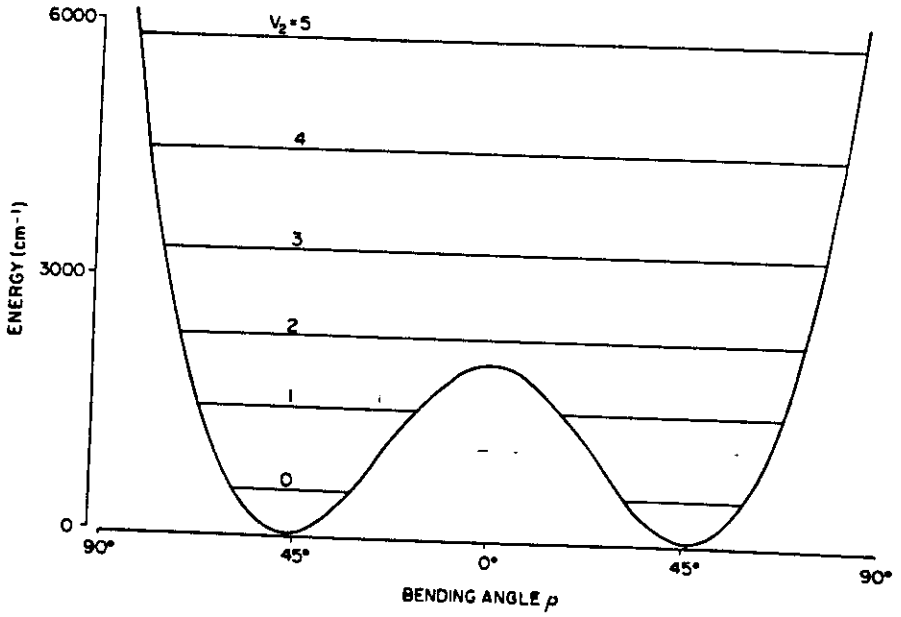


FIG. 3. The experimentally determined effective bending potential energy function for CH_2 in the $v_1 = v_3 = 0$ level of the $\tilde{X}\ ^3B_1$ ground state. Used by permission [48].

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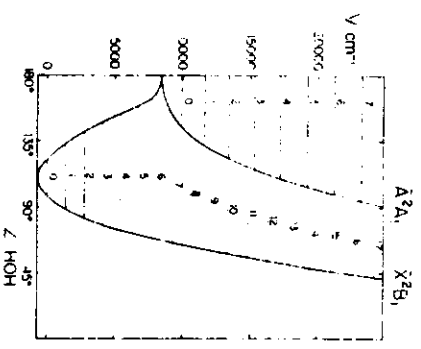


Figure 5. Bending potential curves for the $\tilde{X}\ ^2B_1$ and $\tilde{A}\ ^2A_1$ states of H_2O^+ (cf. the caption for figure 1).

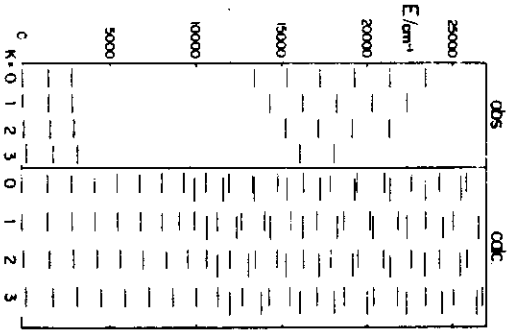


Figure 6. Observed and calculated vibronic level patterns in H_2O^+ (cf. the caption for figure 2); observed levels marked with broken lines are taken from the photoelectron data [9].

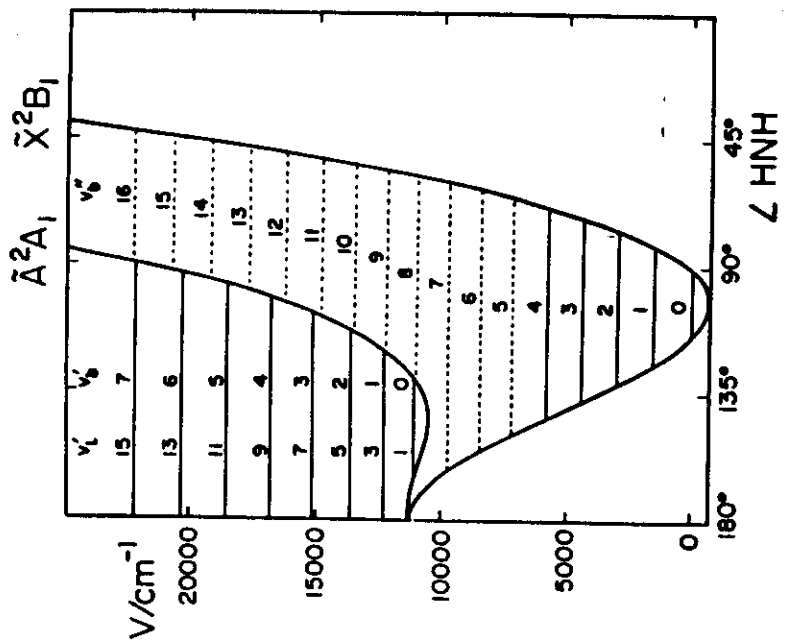


FIG. 4. Bending potential energy curves for the $\tilde{X}\ ^2B_1$ and $\tilde{A}\ ^2A_1$ states of NH_2. The positions of the observed (——) and calculated (---) $K_a = 0$ bending levels are indicated. Vibrational numberings of the excited state levels are given for both linear (v_2') and bent (v_b') notations (adapted from and used by permission [75]).

FIG. 5. served level levels ' om

VIBRATIONAL & ELECTRONIC SPECTRA SIMPLE BECAUSE ALL EL. & FUNDAMENTAL VIBRATIONAL STATES NON-DEGENERATE

ROTATIONAL SPECTRA - COMPLICATED;

ASYMMETRIC TOP .. LEVELS $J_{K_{-1}K_{+1}} = J_\tau$

$$\tau = K_{-1} - K_1$$

SYMMETRY OF THE ROTATIONAL LEVELS DETERMINED BY THE IR OF THE V-GROUP (E, C_2^x, C_2^y, C_2^z)

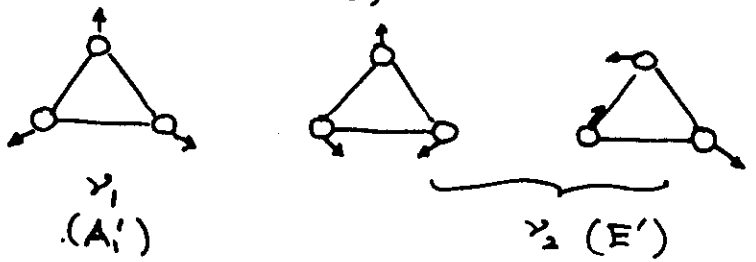
FOR SYMMETRIC BENT ($H_2O, CH_2, ..$) THERE ARE TWO ($I_\alpha = 1/2$) OR MORE ($I_\alpha = 1, ..$; EX. D_2O) MOLECULAR SPECIES (ORTHO, PARA, META, ..)

BENT SYMMETRICAL ($H_3^+, H_3, ...$)

SYMMETRY D_{3h}; VIB. SPECIES: $A_1', A_1'', A_2', A_2'', E', E''$

→ THERE CAN BE BOTH NON-DEG. AND DEGENERATE VIBR. & ELECTRONIC STATES

VIBRATIONS (3N-6 = 3)



VIBR. LEVELS $(v_1 v_2^\ell)$ $\ell = v_2, v_2-2, .., 0$ OR 1

ℓ-DEGENERATE

ℓ - DOUBLING : → SPLITTING OF ℓ-DEG. LEVELS

ROTATIONAL : CORIOLIS COUPLING BETWEEN A NON-DEGENERATE AND A DEGENARATE MODE DUE TO ROTATION ABOUT THE x,y AXES ; ALSO ν_t, ν_t' & R_z

VIBRATIONAL : ANHARMONIC COUPLING BETWEEN A NON-DEG. AND A DEGENERATE MODE

ROTATION : SYMMETRIC TOP

$$E = BJ(J+1) - (B-A)K^2 \rightarrow K\text{-DEGENERACY}$$

K-TYPE DOUBLING : SPLITTING OF ROTATIONAL LEVELS WITH $K = 3n$; $n = 1, 2, \ldots$

DUE TO THE TERM $\mathcal{H}_K = h_3 (J_+^6 + J_-^6)$ $(C_{3v}, \ldots)$

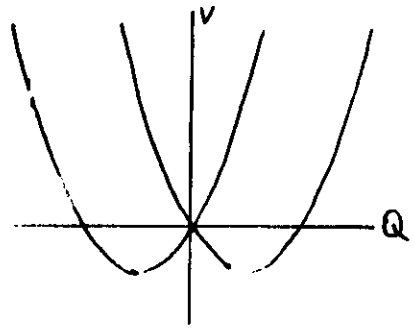
WHICH GIVES MATRIX ELEMENTS OFF-DIAGONAL IN K

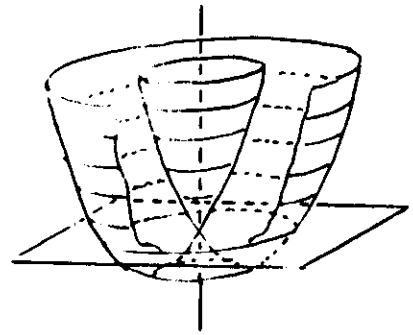
JAHN-TELLER EFFECT

THEOREM: FOR A NON-LINEAR MOL. IN A DEGENERATE ELECTRONIC STATE, THERE EXISTS A DISTORTION OF THE NUCLEI ALONG AT LEAST ONE NON-TOTALLY SYM-METRIC NORMAL COORDINATE THAT RESULTS IN A SPLITTING OF THE POTENTIAL ENERGY FUNCTION SO THAT THE POTENTIAL MINIMUM IS NOLONGER AT THE SYMMETRICAL POSITION

$$\mathcal{H}'_{JT} = \cdots k_i^{+-} Q_+^i + k_i^{-+} Q_-^- \quad \text{LINEAR JT-}$$
$$+ q_i^{-+} Q_-^2 + q_i^{+-} Q_+^2 \quad \text{QUADR. JT-}$$

k_i, q_i CONSTANTS DEPENDING ON THE ELECTRONIC STRUCTURE; $Q_3^i = Q_i^i \pm i Q_i^i$





WITH ONLY LINEAR INTERACTIO

WHEN QUADRATIC TERMS ARE INCLUDED THERE ARE THREE (FOR C_{3v}, D_{3h},) BOWLS SEPARATED BY SADDLE POINTS, ALL OF WHICH ARE JOINED TOGETHER IN THE CENTER BY A CONICAL PEAK.

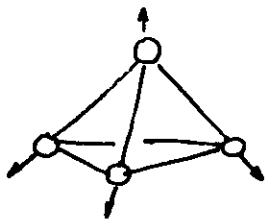
WHEN THE INTERACTION IS WEAK MOLECULE CAN TUNNEL BETWEEN THE BOWLS, FOR STRONG INTER-ACTION MOLECULE BECOMES NON-SYMMETRIC

VERY COMPLICATED SPLITTING & PERTUR... TIES

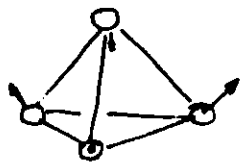
FOUR-ATOMICS ($H_3O^+, CF_3, \ldots, NH_3$)

ONLY C_{3v} SPECIES A_1, A_2, E

VIBRATIONS ($3N-6 = 6$) $2A_1 (\nu_1, \nu_2) + 2E (\nu_3, \nu_4)$



$\nu_1 (A_1)$



$\nu_2 (A_1)$

VIB. LEVELS $(v_1 v_2 v_3^{l_3} v_4^{l_4})$

ESSENTIALLY SAME INTERACTIONS (BUT THERE IS ONLY ONE DEGENERATE VIBRATION) AND STRUCTURE OF ENERGY LEVELS AS IN X_3 + INVERSION POT. SEE HO_3^+

<u>FIVE-ATOMICS</u> (NH_4, ... , CH_4)

ONLY T_d SYMMETRY (C_{3v} AS ABOVE)

VIB. & ELECT. SPECIES ... A_1, A_2, E, F_1, F_2

(1,2 SYM./ANTISYM. σ_d, S_4)

VIBRATIONS ($3N-6=9$) $\nu_1(A_1), \nu_2(E), \nu_3(F_2), \nu_4(F_2)$

VIB. LEVELS $(v_1 v_2^{\ell_2} v_3^{\ell_3 m_3} v_4^{\ell_4 m_4})$

ROTATION SPHERICAL TOP

$$E_J = BJ(J+1)$$

DEGENERACY $(2J+1)^2$

PERTURBATIONS:

$$T^4 = (70)^{1/2} T^4_0 + 5T^4_{+4} + 5T^4_{-4}$$

$$T^6 = (14)^{1/2} T^6_0 - 7T^6_{+4} - 7T^6_{-4}$$

$$T = C[(T^4 \cos\phi + T^6 \sin\phi)\cos\Theta + T^8 \sin\Theta]$$

T_d SYMMETRY

A_1, A_2 ... 1x

E ... 2x

$(T_1, T_2)\ F_1, F_2$ ... 3x

$J = 54$ ... $2J+1 = 109$

FINE STRUCTUR

$5A_1 + 5A_2 + 9E + 13F_1 + 14F_2$ ⇑

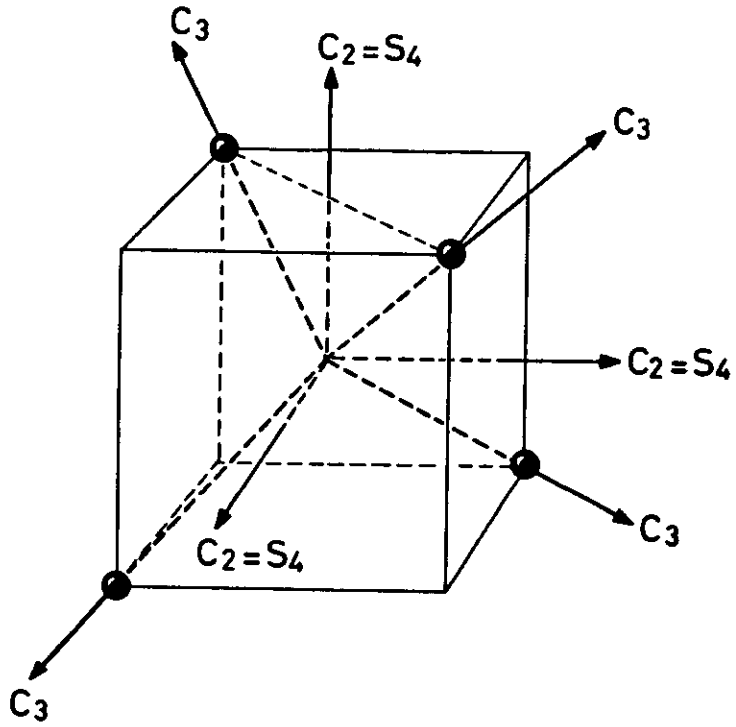
AT LEAST 46 LEVELS EXPECTED

→ ONLY 15-20 LINES OBSERVED (FOR CF_4)

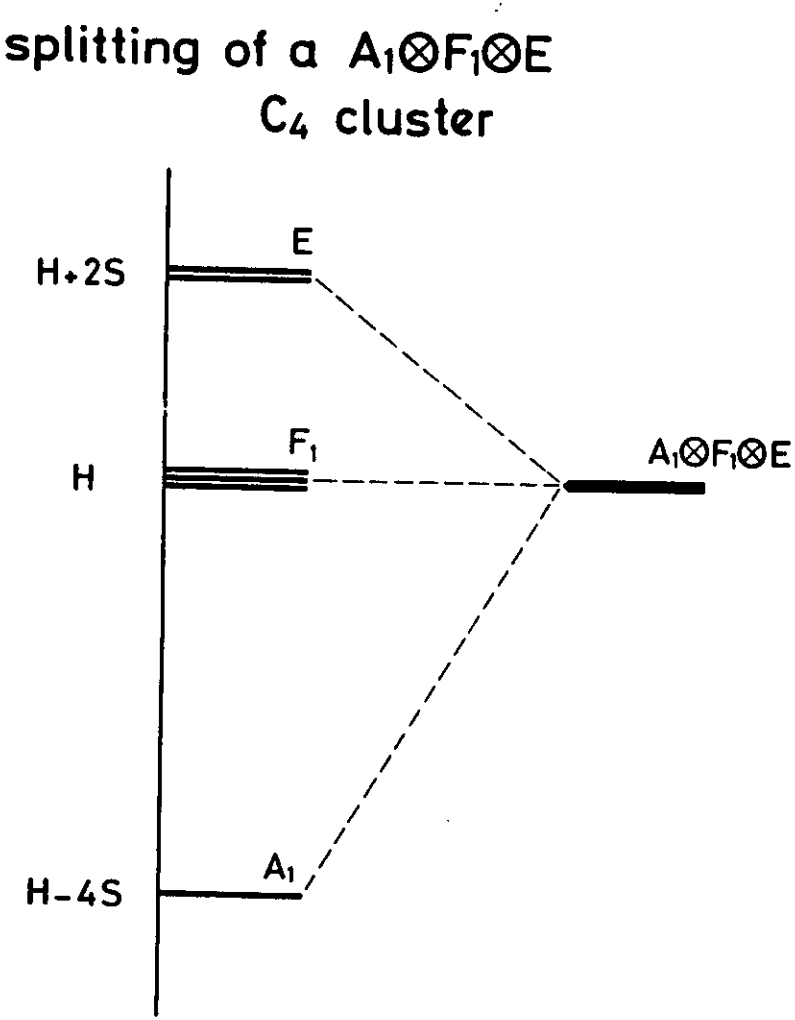
$J = 54$	$K = 47$	$S = 120$ MHz
	48	2.6 MHz
	⋮	
	52	9.4 Hz
	53	9.7 m Hz
	54	3.5 m Hz

SPLITTING OF THE CLUSTERS:

≡ SUPERFINE STRUCTURE



T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	
F_1	3	0	-1	1	-1	(R_x, R_y, R_z)
F_2	3	0	-1	-1	1	(x, y, z)



PRODUCTION METHODS

DISCHARGE
- HALLOW CATHOD
- POSITIVE COLUMN

REACTION
- F ATOMS FROM F_2, CF_4 + He DISCH.
- O FROM O_2 DISCHARGE
- H FROM H_2 OR H_2O

DISCHARGE (USUALLY MICROWAVE)

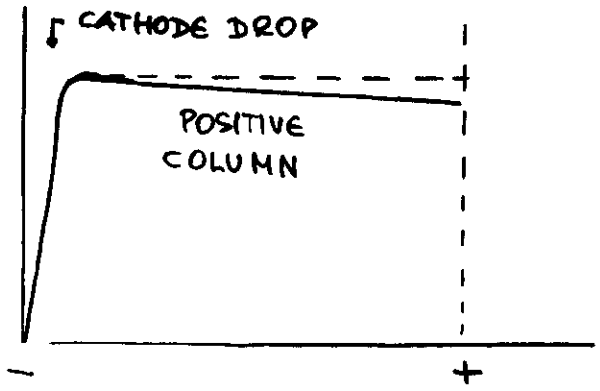
LASER PHOTOLYSIS
- EXCIMER LASER (REMPI)

SURFACE SPUTTERING
- ACCELERATED ATOMIC IONS

ION BEAMS

EXTRACTION FROM AFTERGLOW (PENNING)

CONTROLLED ELECTRON IMPACT OF MOLECULAR (SUPERSONIC) BEAMS



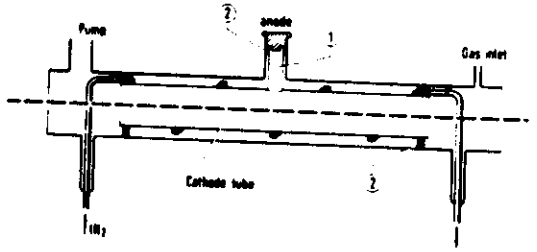


Fig. 1 Glass absorption cell with cold hollow cathode.
1. Glass insert 2. Teflon seals

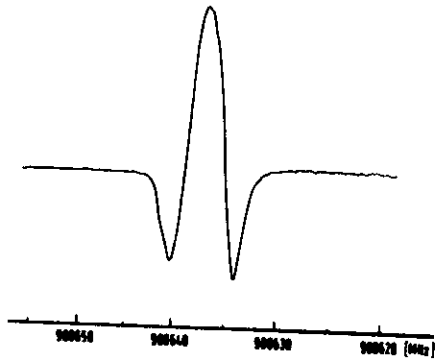


Fig. 2 The J' = 11 ← J = 10 rotational transition of HCO^+ (v = 0) observed using frequency modulation. Integration time 1 s, cell pressure 4 Pa, discharge current 300 mA.

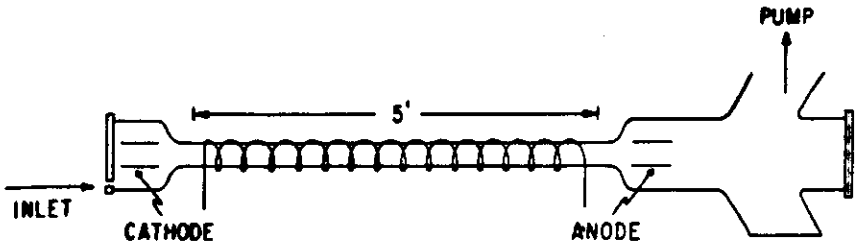
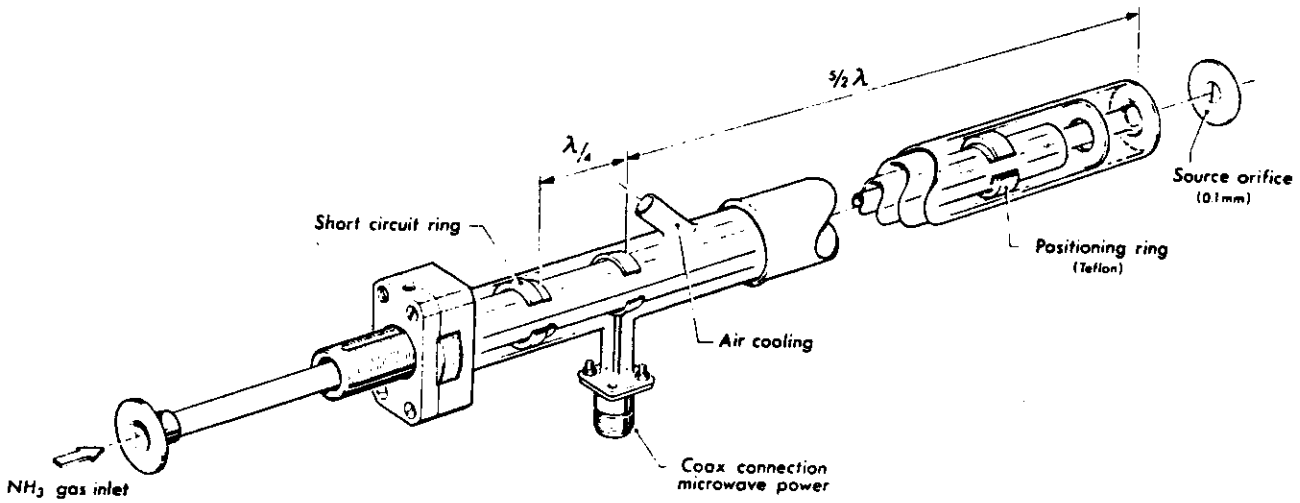
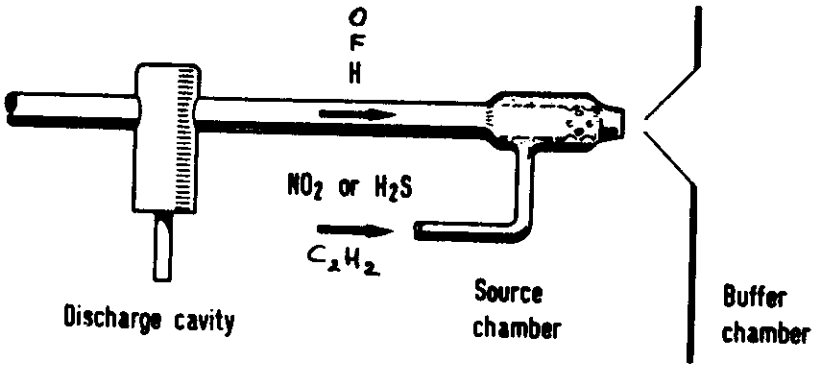
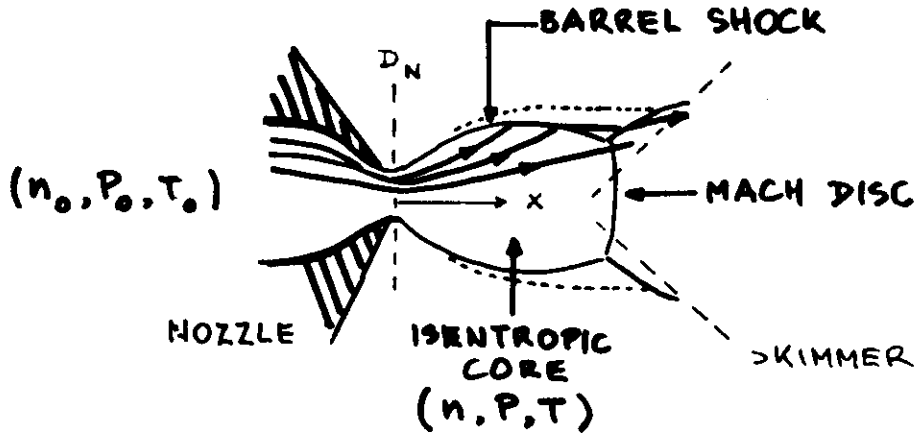


FIG. 1. Diagram of apparatus for the production of molecular ions.





SUPERSONIC NOZZLE BEAMS



ISENTROPIC ($dS = 0$) EXPANSION FROM HYDRODYNAMIC TO FREE MOLECULAR FLOW ($n(x) \propto x^{-2}$). EXPANSION IS SO FAST THAT THE GAS CANNOT EXCHANGE ENERGY WITH WALLS ETC., AND ANISOTROPIC ($T_\parallel, T_\perp$)

RELEVANT QUANTITIES:

SPECIFIC HEAT RATIO $\gamma = C_p/C_v$
(5/3 MONATOMIC, 7/5 DIATOMIC, $\to$ 1 POLYATOMIC)

LOCAL SPEED OF SOUND $a = (\gamma kT/m)^{1/2}$

MOST PROBABLE VELOCITY $\alpha = (2kT/m)^{1/2}$

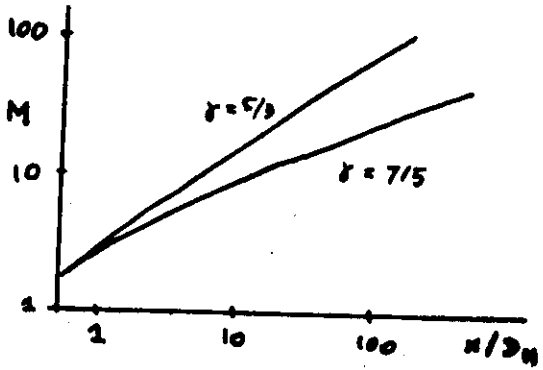
STREAM VELOCITY U

SPEED RATIO $S = U/\alpha$ (U/α_s)

MACH NUMBER $M = U/a = (2/\gamma)^{1/2} S$

$$M = A\left(\frac{x}{D_N}\right)^{\gamma-1} - \frac{1}{2}\left(\frac{\gamma+1}{\gamma-1}\right) / A\left(\frac{x}{D_N}\right)^{\gamma-1}$$

$(A = A(\gamma) \ldots 3.26 - 6.44)$



TERMINAL MACH NUMBER

$$M_T \approx 1.17 Kn_N^{-0.4} = 133 (P_0 D_N)^{0.4} \qquad (Ar)$$

$(Kn_N = \lambda_0 / D_N$; P_0 IN ATM., D_N IN CM)

POSITION MACH DISK $x_M \approx 0.67 (P_0/P_b)^{1/2} D_N$

(P_b - BACKGROUND PRESSURE, BEHIND THE SKIMMER)

TERMINAL STREAM VELOCITY

$$U_N = \left(\frac{2}{\gamma-1}\right)^{1/2} a_0 = \left(\frac{\gamma}{\gamma-1}\right) u_0$$

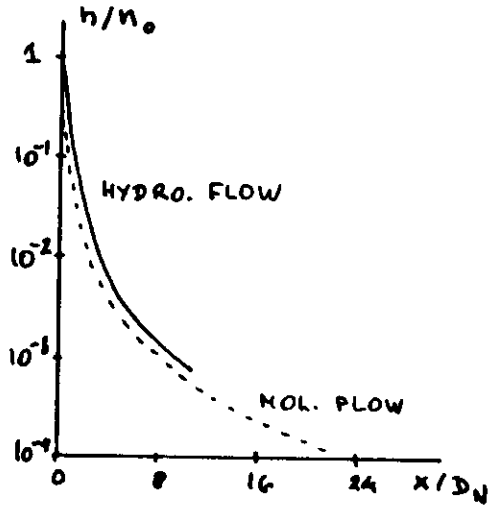
$\rightarrow \sqrt{3}$ FOR MONATOMIC GAS

HIGH INTENSITY

(PRECOLLIMATION, DIRECTED FLOW, LOWERING OF a AND HENCE INCREASE OF M VIA COOLING)

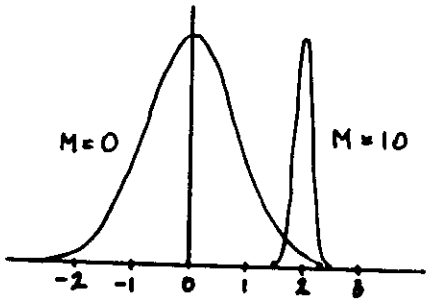
$$\frac{I(0)_M}{I(0)_{OR}} \approx \left(\frac{\gamma}{2} M_s^2 + \frac{3}{2}\right) \qquad (M_s > 4)$$

$$\frac{n}{n_0} = \left[1 + \frac{\gamma-1}{2} M_s^2\right]^{-1/(\gamma-1)} \qquad (\text{FREE JET})$$



NARROW VELOCITY DISTRIBUTION

$$n(v) = v^2 \exp\left[-S^2\left(\frac{v}{v_s} - 1\right)^2\right]$$



(He)

$$\frac{\Delta v}{v} \propto \frac{\alpha_s}{v_s} = \left(\frac{2}{\gamma}\right)^{1/2} M_s^{-1}$$

$$\frac{v_\perp}{v_\parallel} \propto \frac{\alpha_s}{v_s} \propto \left(\frac{2}{\gamma}\right)^{1/2} M_s^{-1}$$

(ANG. SPREAD

$$\frac{v_s}{\alpha_B} = M_s\left[\frac{\gamma}{3 + \frac{3}{2}(\gamma-1)M_s^2}\right] = M_s\left(\frac{\gamma}{3}\frac{T_s}{T_0}\right)^{1/2}$$

$$\rightarrow \left(\frac{2}{3}\frac{\gamma}{\gamma-1}\right)^{1/2} \quad \text{FOR } M_s \rightarrow \infty$$

$$= 1.53 \quad \text{DIATOMIC}$$
$$1.29 \quad \text{MONATOMIC GAS}$$

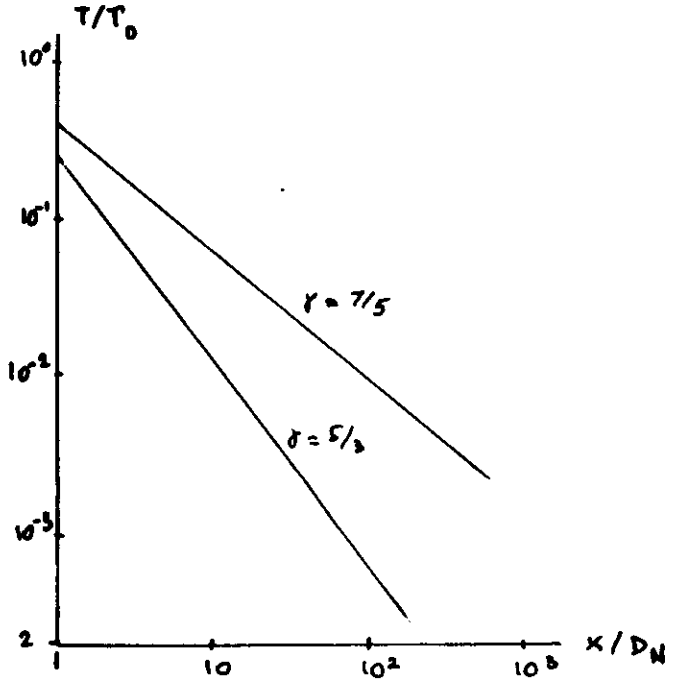
LOW TEMPERATURE

ISENTROPIC REGIME $\left(\frac{\partial T}{\partial v}\right)_s < 0$

CONSERVATION OF ENTHALPY

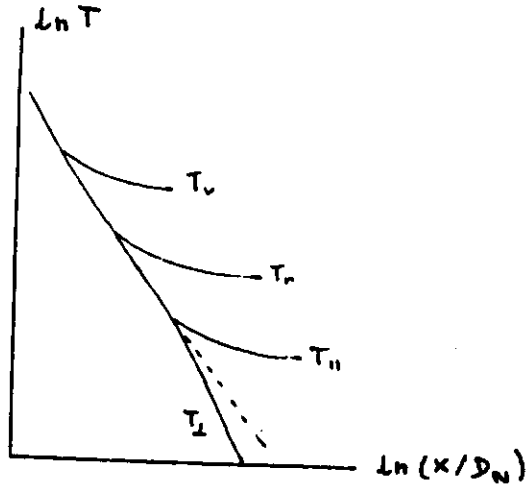
$$h_0 = \frac{1}{2} m \bar{v}^2 + \frac{3}{2} kT_\parallel + \frac{2}{2} kT_\perp + \int_0^{T_r} C_r\, dT + \int_0^{T_v} C_v\, dT$$

$$\frac{T}{T_0} = \left[1 + \left(\frac{\gamma-1}{2}\right)M^2\right]^{-1}$$



$$T(x) \propto x^{-2(\gamma-1)}$$

FULL EXPANSION



$$T_{||} = \frac{1}{2}\frac{m}{k}\left(\frac{U}{S}\right)^2$$

$$\rightarrow \frac{\gamma}{\gamma-1}\frac{T_0}{S^2} \qquad (S \gg 1)$$

$$\propto T_0^{1.3}(P_0 D_N)^{-1.0} \qquad He, Ne, Ar$$

$$\propto T_0^{0.8}(P_0 D_N)^{0.6} \qquad SF_6, \ldots$$

CONDENSATION PHENOMENA

- FORMATION OF CLUSTERS
  ($(H_2)_n$, NeAr, ...)

SEEDED BEAMS

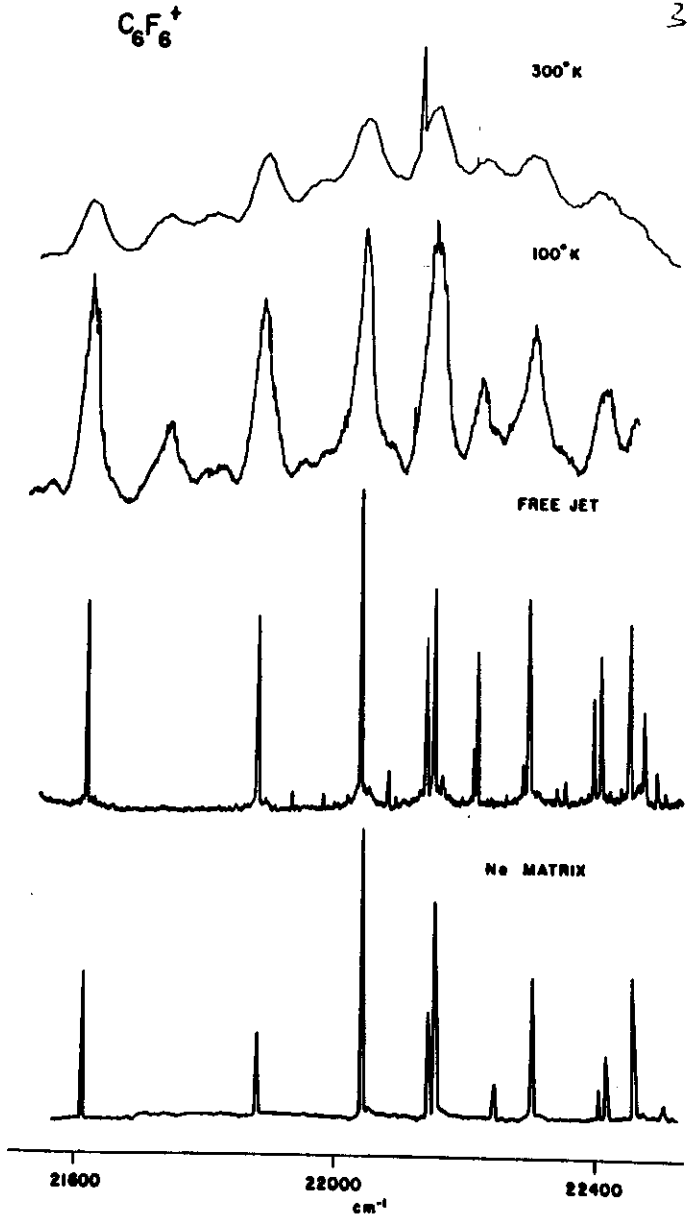


Figure 2.

Laser excitation spectra of $C_6F_6^+$ taken under a variety of conditions. Preceeding upward from the bottom (i) $C_6F_6^+$ in a Ne matrix at 4°K, (ii) $C_6F_6^+$ produced via 2-photon ionization by an ArF laser in a free jet expansion, (iii) $C_6F_6^+$ produced by Penning ionization with the flow system at liquid N_2 temperature, (iv) same as (iii) except flow system at room temperature. The Ne matrix spectrum has been shifted in absolute frequency so that its origin coincides with those of the gas phase spectra.

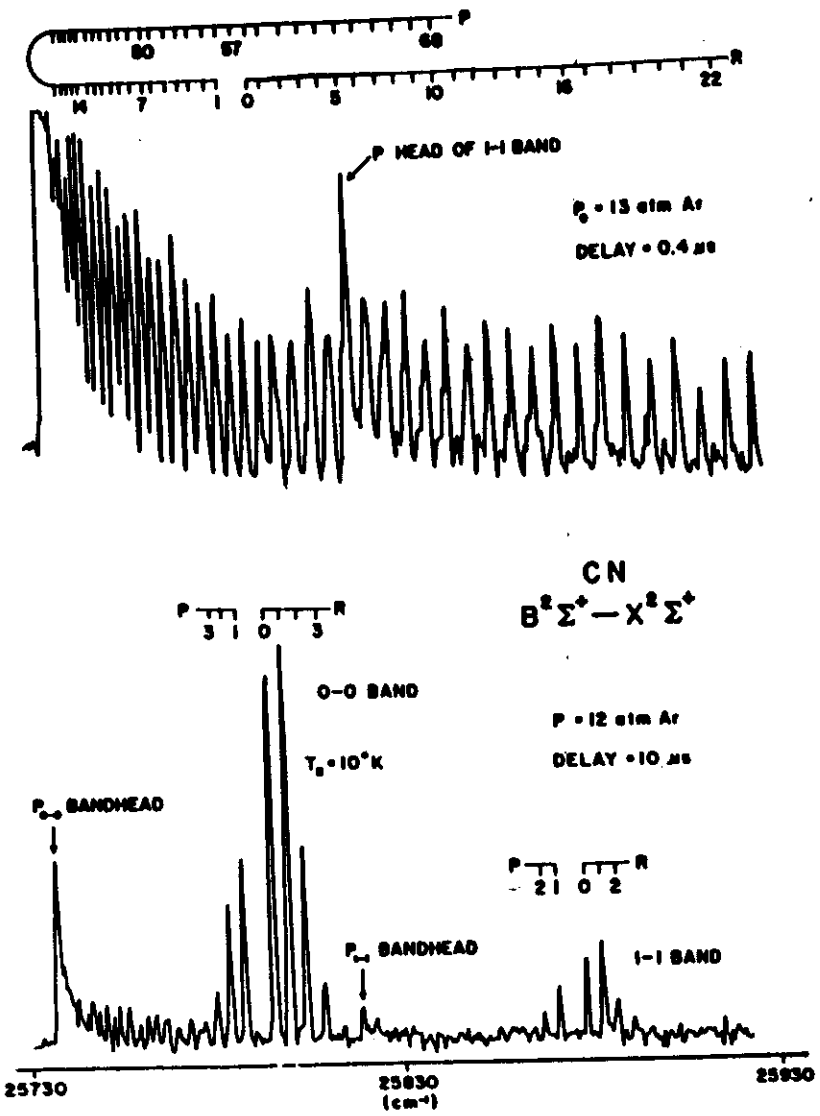


Fig. 6. Laser-induced fluorescence spectra of the CN ... induced by the ArF laser photolysis of BrCN in a...

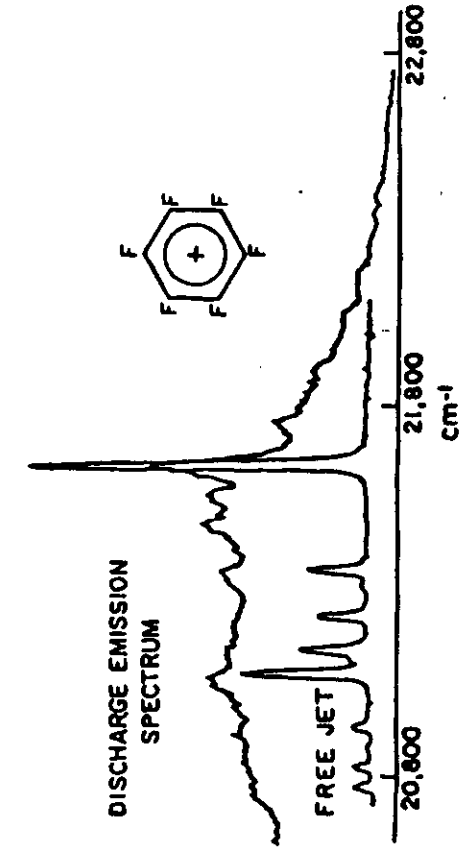


Fig. 3. Wavelength Resolved Emission Spectra of $C_6F_6^+$. The top spectrum was obtained by electron impact ionization and excitation of C_6F_6 in a cell at roughly 100 millitorr pressure. The lowest trace was obtained from $C_6F_6^+$ in a supersonic jet, laser excited.

equilibrium configuration, from D_{6h} symmetry by the Jahn-Teller ... based upon these studies. Fig. 4 shows in some detail

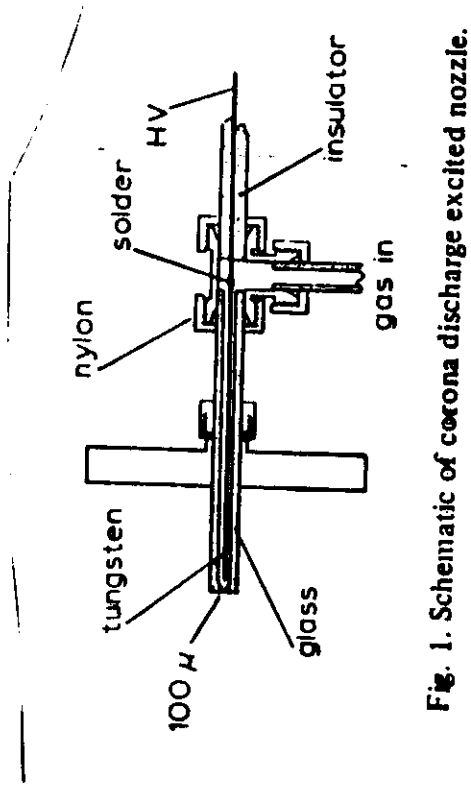


Fig. 1. Schematic of corona discharge excited nozzle.

DETECTION SPECTROSCOPIES

- EMISSION (VISIBLE, UV)
  - HALLOW CATHODE DISCHARGE
  - ELECTRON IMPACT FLUORESCENCE
  - AFTERGLOW PENNING IONIZATION
  - CHEMILUMINESCENCE
  - ELECTRON IMPACT IONIZATION OF MOL. BEAM
  - (- LASER INDUCED FLUORESCENCE)
- PHOTODETACHMENT (NEG. IONS)
- PHOTOELECTRON
- MATRIX ISOLATION
- MICROWAVE + BEAM MASER + ESR
- FAR INFRARED (ESP. LIGHT SPECIES
- RADIO ASTRONOMY
- LASER MAGNETIC/ELECTRIC RESONANCE
- IR LASER - COLOUR CENTER
  - DIODE
  - DIFFERENCE FREQUENCY
- LASER DOPPLER (ION BEAMS)
- RF-SPECTROSCOPY OF TRAPPED IONS
- LIF

MODULATION TECHNIQUES:

ZEEMAN (PARAMAGNETIC SPECIES ONLY)
FREQUENCY
CONCENTRATION
VELOCITY (IONS ONLY)

REACTIVE PRODUCTION (EXAMPLES)

$X^2\Pi$	OH	$H + NO_2 \rightarrow OH + NO$
$X^2\Pi$	SH	$H + H_2S \rightarrow SH + H_2$
$X^2\Pi$	IO	$O + I_2 \rightarrow IO + I$
$X^2\Pi$	CH	$H + C_2H_2$
$\tilde{X}^2A_1$	HCO	$F + H_2CO$

DISCHARGE

$X^3\Sigma^-$	OH^+	$H_2 + O_2 + He$
$X^2\Pi$	NH^+	$H_2 + N_2 + He$
$X^3\Sigma, a^1\Delta$	NH	NH_3
$X^1\Sigma$	CF	CF_4, C_2F_4, CH_3F
$X^2\Sigma$	CO^+	$H_2 + CO$
$X^2\Pi$	SiCl	$SiCl_4 + Ar$
$X^2\Pi$	HBr^+	$HBr + He$
$X^2\Pi$	HCl^+	$HCl + He$
$X^2\Sigma$	N_2H^+	$H_2 + N_2$
	ArH^+	$Ar + H_2$
	KrH^+	$Kr + H_2$
	H_2^+	H_2
	H_3^+	H_2 $(H_2 + H_2^+ \rightarrow H_3^+ + H)$
$X^1\Sigma$	HCO^+	$H_2 + CO$
$\tilde{A}^2A_1$	NH_2	NH_3
$\tilde{X}^3B_1$	CH_2	$CH_4 + CF_4$
	$SiCl_2$	$SiCl_4 + Ar$
	H_3O^+	$H_2 + O_2$
	NH_4^+	NH_3
$^2A_1$	NH_4	NH_3 $(NH_4^+ + e)$