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PEAD – FOR THE CALCULATION OF PHOTOELECTRON ANGULAR DISTRIBUTIONS OF LINEAR MOLECULES

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PROGRAM SUMMARY

Title of program: PEAD

Catalogue number: AAXD

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Computer: NAS 7000; *Installation:* SERC, Daresbury Laboratory

Other machines on which program tested: CRAY-1S, Amdahl 470/V8

Programming language used: FORTRAN 77

High speed storage required: 152000 32-bit words

Peripherals used: card reader, line printer, disk file

No. of lines in program and test deck: 658

Keywords: photoionisation, photoelectron angular distribution, asymmetry parameter β, rotationally resolved, adiabatic nuclei approximation, Boltzmann distribution

Nature of physical problem

PEAD takes photoionisation dipoles and calculates rotationally averaged and rotationally resolved photoionisation cross section parameters σ and β [1,2]. These are then used to give thermally averaged parameters σ_Q, σ_S, β_Q and β_S for a given initial temperature.

Method of solution

The photoionisation cross section parameters, σ and β, are calculated using the adiabatic nuclei approximation for transitions between a range of rotational states. These are then thermally averaged using a Boltzmann distribution of initial rotational states.

Restrictions on the complexity of the problem

The program assumes the parent molecule is linear and that the whole system remains in a singlet spin state.

Typical running time

Data dependent. For a 3 channel problem on the NAS 7000, about 40 sets of transition dipoles can be analysed per second.

References

[1] Y. Itikawa, Chem. Phys. 28 (1978) 461.
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LONG WRITE-UP

1. Introduction

Low-energy photoelectron spectra contain a wealth of information about both the electronic structure of a molecular target and the interaction of the ejected electron with the resulting ion. For a linear molecular target in a singlet spin symmetry, the fully resolved process can be represented:

$$h\nu(E_r, l_r = 1, m_r) + \mathrm{X}(^1\Lambda_i, v_i, N_i) \rightarrow \mathrm{X}^+(^2\Lambda_f, v_f, N_f) + \mathrm{e}^-(E_e), \quad (1)$$

where $h\nu$ represents a photon of frequency ν and energy E_r. The photon total angular momentum is given by l_r and its polarisation by m_r ($=0$ for linear polarisation, $=\pm 1$ for circular polarisation). $\Lambda_{i/f}$ ($=0, 1, 2, \ldots$) represents the spatial electronic state of the target/ion (Σ, Π, Δ, ...); $v_{i/f}$ denotes the vibrational state of the target/ion which occupy rotational level $N_{i/f}$ respectively. The ejected electron has kinetic energy E_e.

For linear polarised light, the angularly resolved cross section for this process can be written

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right) = \frac{\sigma}{4\pi}(1 + \beta P_2(\cos\theta)) \quad m_r = 0, \quad (2)$$

where σ is the isotropic cross section and β the asymmetry parameter. Ω is the solid angle about the direction of propagation of the incoming light. In (2) θ is the angle between the direction of the electric vector and that of the ejected electron. For circularly polarised light, averaging over $m_r = \pm 1$ gives

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right) = \frac{\sigma}{4\pi}(1 - \tfrac{1}{2}\beta P_2(\cos\theta)), \quad (3)$$

where now θ is the angle between the direction of the incident photon beam and that of the ejected electron.

While changes in vibrational state ($v_i \rightarrow v_f$) are largely determined by the relative position of the target and ion potential curves, the rotationally resolved photoionisation parameters are highly sensitive to the details of the interaction between the residual ion and the escaping electron. The rotational structure is usually dominated by transitions with ΔN ($= N_f - N_i$) equals 0 (Q branch), +2 (S branch) and −2 (O branch). Ab initio calculations on the photoionisation of H_2 have shown that the value of β_S, in particular, is highly sensitive to the level of approximation used [1-3]. Photoionisation experiments usually involve the target molecule in a range of rotational states determined by the experimental temperature. Thus for a direct comparison of theory with observation it is not only necessary to calculate rotational resolved photoionisation parameters, but also to thermally average them.

The program presented here takes photoionisation transition dipoles either in the usual or momentum transfer form and computes σ and β parameters as a function of initial and final rotational state. These are then averaged over the initial rotational population given by a Boltzmann distribution to give photoionisation parameters that can be directly compared with experiment. The program is independent of the theoretical model used to calculate the transition dipole matrix elements.

2. Method

The total cross section, σ, and asymmetry parameter, β, can be written

$$\sigma(N_i \rightarrow N_f) = 4\pi^2 a_0^2 \alpha f A_0(N_i \rightarrow N_f), \quad (4)$$

$$\beta(N_i \rightarrow N_f) = A_2(N_i \rightarrow N_f)/A_0(N_i \rightarrow N_f), \quad (5)$$

where α is the fine structure constant, a_0 is the Bohr radius of the hydrogen atom and f equals E_r, the energy of the incident photon, in the dipole length approximation and $1/E_r$ in the dipole velocity approximation. Here and elsewhere the explicit dependence on the vibrational state of the target and ion have been omitted. The coefficients A_L are given by [2,4]

$$A_L(N_i \rightarrow N_f) = (-1)^L(2L+1)\begin{pmatrix} 1 & 1 & L \\ m_r & -m_r & 0 \end{pmatrix}(2N_f + 1)$$

$$\sum_{l,\,l'} (-\mathrm{i})^{l-l'}\,\mathrm{e}^{\mathrm{i}(\sigma_l-\sigma_{l'})}[(2l+1)(2l'+1)]^{1/2} \times \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \sum_{N_\mathrm{t}} (-1)^{N_\mathrm{t}} \begin{pmatrix} N_\mathrm{f} & N_\mathrm{i} & N_\mathrm{t} \\ -\Lambda_\mathrm{f} & \Lambda_\mathrm{i} & \Delta\Lambda \end{pmatrix}^2 \begin{Bmatrix} l & l' & L \\ 1 & 1 & N_\mathrm{t} \end{Bmatrix} \times D^{N_\mathrm{t}}(l)\,D^{N_\mathrm{t}}(l')^{*}, \tag{6}$$

where the 3- and 6-j symbols are as defined by Brink and Satchler [5] and σ_l is the Coulomb phase. The sums over l, l' run over all the possible orbital angular momenta of the ejected electron. For molecules, l is not a good quantum number and this sum has to be truncated in actual calculations. The dipole matrix elements in (6) are defined using the momentum transfer formalism of Fano and Dill [6]

$$D^{N_\mathrm{t}}(l) = \sum_{\lambda} (-1)^{\lambda}(2N_\mathrm{t}+1)^{1/2} \begin{pmatrix} 1 & l & N_\mathrm{t} \\ -\lambda & m & \Delta\Lambda \end{pmatrix} \times d_{\lambda}^{(-)}(l,\, m), \tag{7}$$

$$d_{\lambda}^{(-)}(l,\, m) = \left(\frac{4\pi}{3}\right)^{1/2} \left\langle \Psi_{lm}^{(-)} \middle| \sum_i g_i Y_{1\lambda}(\hat{r}_i) \middle| \Psi_0 \right\rangle, \tag{8}$$

where Ψ_0 is the target wavefunction and $\Psi^{(-)}$ is the wavefunction of the ion plus ejected electron with partial wave l, m. The minus signifies that the wavefunction has been transformed to outgoing boundary conditions [7]. The operator g_i is r_i in the dipole-length and $\partial/\partial r_i$ in the dipole-velocity approximation. The matrix element is taken over all electronic coordinates. For vibrationally resolved calculations the integration is also over the vibrational mode(s), otherwise the transition dipoles are a function of the relative positions of the fixed nuclei.

If the molecule is taken to be a rigid rotor with rotational constant B, then the initial population of states is given by

$$p(N_\mathrm{i}) = f_\mathrm{i}/z, \tag{9}$$

$$f_\mathrm{i} = (2I_\mathrm{N}+1)(2N_\mathrm{i}+1)\,\mathrm{e}^{-N_\mathrm{i}(N_\mathrm{i}+1)B/kT}, \tag{10}$$

$$z = \sum_{N_\mathrm{i}} f_\mathrm{i}, \tag{11}$$

where k is Boltzmann's constant and I_N is the nuclear spin state of the molecule. For $\mathrm{D}_{\infty\mathrm{h}}$ systems this state usually depends on whether N_i is even or odd. The thermally averaged parameters are given by

$$x_A = \sum_{N_\mathrm{i}} p(N_\mathrm{i})\,x(N_\mathrm{i} \to N_\mathrm{f}), \qquad x = \sigma,\ \beta, \qquad A = \mathrm{Q} \ \text{ if } \ N_\mathrm{f} = N_\mathrm{i}, \quad = \mathrm{S} \ \text{ if } \ N_\mathrm{f} = N_\mathrm{i}+2. \tag{12}$$

For Λ_i equal Λ_f, the adiabatic nuclei approximation gives [4]

$$(2N_\mathrm{i}+1)\,\sigma(N_\mathrm{i} \to N_\mathrm{f}) = (2N_\mathrm{f}+1)\,\sigma(N_\mathrm{f} \to N_\mathrm{i}), \tag{13}$$

$$\beta(N_\mathrm{i} \to N_\mathrm{f}) = \beta(N_\mathrm{f} \to N_\mathrm{i}),$$

and hence $\beta_\mathrm{Q} = \beta_\mathrm{S}$.

Rotationally averaged parameters can be defined in a similar fashion using

$$\bar{A}_L = (-1)^L(2L+1) \begin{pmatrix} 1 & 1 & L \\ m_\mathrm{r} & -m_\mathrm{r} & 0 \end{pmatrix} \sum_{l,\,l'} (-\mathrm{i})^{l-l'}\,\mathrm{e}^{\mathrm{i}(\sigma_l-\sigma_{l'})}[(2l+1)(2l'+1)]^{1/2} \times \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \sum_{N_\mathrm{t}} (-1)^{N_\mathrm{t}} \begin{Bmatrix} l & l' & L \\ 1 & 1 & N_\mathrm{t} \end{Bmatrix} D^{N_\mathrm{t}}(l)\,D^{N_\mathrm{t}}(l')^{*} \tag{14}$$

and eqs. (4) and (5) or the relationships

$$\bar{\sigma} = \sum_{N_\mathrm{f}} \sigma(N_\mathrm{i} \to N_\mathrm{f}) \tag{15}$$

$$\bar{\beta} = \sum_{N_\mathrm{f}} \sigma(N_\mathrm{i} \to N_\mathrm{f})\,\beta(N_\mathrm{i} \to N_\mathrm{f})/\bar{\sigma} \tag{16}$$

The resulting parameters are independent of N_i in the adiabatic nuclei approximation.

3. Program organisation and data input

3.1. Organisation

PEAD reads control data using NAMELIST input from unit 5, and channel and dipole data from stream NFTD. The program loops over input from both streams until end of file marks are reached; this allows batches of transition dipoles to be processed and thermally averaged results for several temperatures to be obtained in one run.

PEAD is composed of the following subroutines:

MAIN controls i/o and the flow of the calculation.
PASCAL creates an array of Binomial coefficients for calculating 3-j symbols.
CPHAZ computes Coulomb phases [8].
TPOP computes the fractional populations of eq. (9).
TRANSD transforms the transition dipoles to the momentum transfer form, see eq. (7).
ALBAR computes $\overline{A}_L$, see eq. (14); $\bar{\sigma}$ and $\bar{\beta}$ are also computed using eqs. (15) and (16) as a check.
ALNINF computes $A_L(N_i \rightarrow N_f)$, see eq. (6).
TAV computes thermally averaged parameters, eq. (12).
THREEJ 3-j symbol routine.

For efficiency, the 6-j and most of the 3-j symbols used in ALBAR and ALNINF have been evaluated explicitly.

3.2. Input from unit 5

Control input is read using NAMELIST /INPUT/ from unit 5. PEAD will continue to look for NAMELIST data until the end of file is reached. As the unit NFTD is rewound each time, this allows the dipoles to be processed for several sets of control data, e.g. temperature or polarisation. Alternatively, the unit associated with NFTD can be changed allowing a new set of dipoles to be processed. Defaults for the input data are given in parenthesis:

MR [0] Polarisation of the light ($=0$ for z, ± 1 for x–y).
ISYM [0] $=0$ for a molecule with $C_{\infty v}$ symmetry
$=1$ for a molecule with $D_{\infty h}$ symmetry.
NIMIN [0] Minimum value of N_i to be considered.
NIMAX [3] Maximum value of N_i to be considered.
WEVEN [1.0] $2I+1$ for the even rotational states.
WODD [1.0] $2I+1$ for the odd rotational states.
NTRAN [4] Maximum value of ΔN to be considered.
NFTD [11] Input stream for transition dipole data.
IVEL [0] $=0$ for the dipole-length approximation.
$=1$ for the dipole-velocity approximation.
IBUG [0 on the first pass and then -1] Print flag:
-1 minimal output,
0 usual, 1 detailed, 2 debug level.
IMOM [0] $=0$ Dipoles read in momentum transfer form $D^N(l)$, see eq. (7).
$=1$ Dipoles read as $d_\lambda^{(-)}(l, m)$, eq. (8), and transformed.
TEMP [0.0] If >0.0, temperature in K for the thermal average.
BROT Rotational constant, B, in cm^{-1}.
MI [0] Λ_i.
MF [0] Λ_f.

Note that if NIMIN $\neq 0$ or NIMAX is too small, then inaccurate thermal averages may result. To perform a calculation on just ortho or para species, the relevent WEVEN/WODD may simply be set to zero.

3.3. Input from unit NFTD

The following lines of input are read from stream NFTD:

1. NCHAN,(LCHL(I),I = 1,NCHAN) [FORMAT(14I5)]
   where NCHAN is the total number of channels and LCHL holds the l values in ascending order.
2. If IMOM = 1 only, (MU(I),I = 1,NFSTAT) [FORMAT(14I5)]
   where MU holds the values of λ for the dipoles in the order in which they are read. NFSTAT = 3, unless $\Lambda_i = 0$ when NFSTAT = 2.
3. NV,EE,EPHOT [FORMAT(I5,2E18.10)]
   where NV is a vibrational label (used only for print purposes), EE is E_e, the kinetic energy of the ejected electron in E_h, and EPHOT is E_r, the photon energy in E_h.
4. If IMOM = 0, then read NCHAN records of

(DIPT(J),J = 1,3) [FORMAT(4E18.10)]
where DIPT are the momentum transfer dipoles $D^N(l)$ with $J = N - l + 2$.

Else if IMOM $\neq 0$, then read NFSTAT records of
(DIPI(I),I = ID,NCHAN)
[FORMAT(4E18.10)]
where DIPI are the dipole $d_\lambda^{(-)}(l, m)$ and ID is such that only the physical dipoles with $l \geqslant m$ are read.

Both sets of dipoles are complex and must be ordered on increasing l, the partial wave of the ejected electron.

PEAD loops over input 3 and 4 until the end of file is reached.

3.4. Test output

Test data for PEAD have been prepared using transition dipoles calculated using the R-matrix method for the photoionisation of H_2 with a fixed bondlength of $1.4a_0$ [9].

Acknowledgement

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References

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[3] Y. Itikawa, Comments At. Mol. Phys. (1987) in press.
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[5] D.M. Brink and G.R. Satchler, Angular Momentum, 2nd ed. (Clarendon Press, Oxford, 1968).
[6] V. Fano and D. Dill, Phys. Rev. A6 (1972) 185.
[7] P.G. Burke, in: Atomic and Molecular Collision Theory, ed. F.A. Gianturco (Plenum, New York, 1982) p. 69.
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TEST RUN OUTPUT

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  PHOTO-ELECTRON ANGULAR DISTRIBUTION PROGRAM:

  POLARISATION DIRECTION, MR =  0
  HOMO/HETRO SYMMETRY FLAG, ISYM =  1
  PRINT FLAG, IBUG =  1
  ELECTRONIC ANGULAR MOMENTUM OF TARGET, MI =   0
  ELECTRONIC ANGULAR MOMENTUM OF ION,    MF =   0
  MINIMUM INITIAL ROTATIONAL STATE, NIMIN =  0
  MAXIMUM INITIAL ROTATIONAL STATE, NIMAX =  3
  MAXIMUM CHANGE IN ROTATIONAL STATE, NTRAN =  6
  WEIGHTING FOR EVEN ROTATION LEVELS, WEVEN =  1.0
  WEIGHTING FOR ODD  ROTATION LEVELS, WODD  =  3.0
  STREAM FOR DIPOLE INPUT, NFTD = 11
  DIPOLES IN LENGTH APPROXIMATION, IVEL =  0
  DIPOLES TO BE TRANSFORMED TO THE MOMENTUM TRANSFER FORMALISM

  THERMAL AVERAGING WITH TEMP =  300.00 K
  ROTATIONAL CONSTANT, BROT =   0.6080000D+02 CM-1

  EFFECTIVE PARTITION FUNCTION USING NI = 0 TO     3, ZEFF = 7.090038D+00
  CONVERGED PARTITION FUNCTION USING NI = 0 TO     8, Z    = 7.145662D+00
  NI =  0 RELATIVE POPULATION 1.410430D-01
  NI =  1 RELATIVE POPULATION 6.802642D-01
  NI =  2 RELATIVE POPULATION 1.085356D-01
  NI =  3 RELATIVE POPULATION 7.015724D-02

  CHANNEL DATA: NUMBER OF L VALUES =  3
  L =  1  3  5
  DIPOLES ORDERED BY MU =  0  1

  VIBRATIONAL STATE =  0
  PHOTON         ENERGY = 6.249956D-01 HARTREE, = 7.290187D+02 ANGSTROM
  PHOTOELECTRON ENERGY = 2.419000D-02 HARTREE, = 6.582584D-01 E.V.

  DIPOLES:
 0.14978233940D+01  0.36962682890D+00  0.87542655710D-02  0.33199781120D-02 -0.72737493990D-04  0.94199340380D-05
  DIPOLES:
 0.14596902590D+01 -0.33662268060D+00  0.89164627270D-02  0.57916448610D-02 -0.62555729600D-04 -0.96003617940D-05
  DIPOLES:
-0.25502738677D+01  0.17529424135D+00  0.00000000000D+00  0.00000000000D+00  0.31135571485D-01  0.57665025677D+00
-0.15263110295D-01 -0.83649638817D-02  0.00000000000D+00  0.00000000000D+00 -0.16374376653D-02 -0.28523536680D-02
 0.11437693710D-03  0.36763326317D-05  0.00000000000D+00  0.00000000000D+00  0.59243491345D-05  0.16110670153D-04
```

```
   A0-BAR     = 2.289478D+00,    A2-BAR    = 4.388578D+00
   SIGMA-BAR = 1.154358D+01 MB, BETA-BAR = 1.916847D+00
NI =  0 NF =  0 A0     = 2.178208D+00,    A2    = 4.356417D+00
                 SIGMA = 1.098256D+01 MB, BETA = 2.000000D+00
NI =  0 NF =  2 A0     = 1.112660D-01,    A2    = 3.216038D-02
                 SIGMA = 5.610048D-01 MB, BETA = 2.890406D-01
NI =  0 NF =  4 A0     = 3.610073D-06,    A2    = 1.526227D-06
                 SIGMA = 1.820205D-05 MB, BETA = 4.227691D-01
NI =  0 NF =  6 A0     = 9.821720D-11,    A2    = 3.777585D-11
                 SIGMA = 4.952127D-10 MB, BETA = 3.846154D-01

NI =  0 SIGMA-BAR = 1.154358D+01 MB, BETA-BAR = 1.916847D+00

NI =  1 NF =  1 A0     = 2.222715D+00,    A2    = 4.369281D+00
                 SIGMA = 1.120696D+01 MB, BETA = 1.965741D+00
NI =  1 NF =  3 A0     = 6.676118D-02,    A2    = 1.929691D-02
                 SIGMA = 3.366109D-01 MB, BETA = 2.890438D-01
NI =  1 NF =  5 A0     = 2.005641D-06,    A2    = 8.479215D-07
                 SIGMA = 1.011248D-05 MB, BETA = 4.227683D-01
NI =  1 NF =  7 A0     = 5.288619D-11,    A2    = 2.034084D-11
                 SIGMA = 2.666530D-10 MB, BETA = 3.846154D-01

NI =  1 SIGMA-BAR = 1.154358D+01 MB, BETA-BAR = 1.916847D+00

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                 SIGMA = 1.114285D+01 MB, BETA = 1.975388D+00
NI =  2 NF =  4 A0     = 5.722343D-02,    A2    = 1.654002D-02
                 SIGMA = 2.885215D-01 MB, BETA = 2.890428D-01
NI =  2 NF =  6 A0     = 1.640967D-06,    A2    = 6.937493D-07
                 SIGMA = 8.273783D-06 MB, BETA = 4.227685D-01
NI =  2 NF =  8 A0     = 4.230895D-11,    A2    = 1.627267D-11
                 SIGMA = 2.133224D-10 MB, BETA = 3.846154D-01

NI =  2 SIGMA-BAR = 1.154358D+01 MB, BETA-BAR = 1.914037D+00

NI =  3 NF =  3 A0     = 2.207880D+00,    A2    = 4.364993D+00
                 SIGMA = 1.113217D+01 MB, BETA = 1.977007D+00
NI =  3 NF =  5 A0     = 5.298458D-02,    A2    = 1.531480D-02
                 SIGMA = 2.671491D-01 MB, BETA = 2.890426D-01
NI =  3 NF =  7 A0     = 1.472661D-06,    A2    = 6.225948D-07
                 SIGMA = 7.425180D-06 MB, BETA = 4.227686D-01
NI =  3 NF =  9 A0     = 3.733143D-11,    A2    = 1.435824D-11
                 SIGMA = 1.882256D-10 MB, BETA = 3.846154D-01

NI =  3 SIGMA-BAR = 1.154358D+01 MB, BETA-BAR = 1.913235D+00


   SIGMA-Q = 1.116311D+01 MB,  BETA-Q = 1.972410D+00
   SIGMA-S = 3.581674D-01 MB,  BETA-S = 2.890432D-01


   THERMAL AVERAGING WITH TEMP =  150.00 K
   ROTATIONAL CONSTANT, BROT =   0.6080000D+02 CM-1

   VIBRATIONAL STATE =  0
   PHOTON          ENERGY = 6.249956D-01 HARTREE, = 7.290187D+02 ANGSTROM
   PHOTOELECTRON ENERGY = 2.419000D-02 HARTREE, = 6.582584D-01 E.V.

   SIGMA-Q = 1.114428D+01 MB,  BETA-Q = 1.975306D+00
   SIGMA-S = 3.952611D-01 MB,  BETA-S = 2.890429D-01
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