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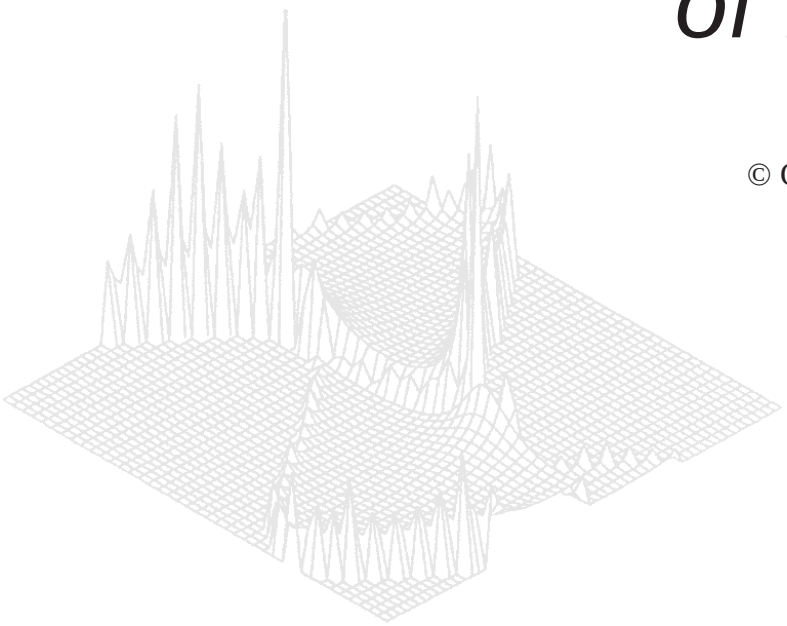

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Deconvolution of Overlapping Features in Electron Energy-loss Spectra: Determination of Absolute Differential Cross Sections for Electron-impact Excitation of Electronic States of Molecules*

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Abstract

A set of three computer programs is reported which allow for the deconvolution of overlapping molecular electronic state structure in electron energy-loss spectra, even in highly perturbed systems. This procedure enables extraction of absolute differential cross sections for electron-impact excitation of electronic states of diatomic molecules from electron energy-loss spectra. The first code in the sequence uses the Rydberg–Klein–Rees procedure to generate potential energy curves from spectroscopic constants, and the second calculates Franck–Condon factors by numerical solution of the Schrödinger equation, given the potential energy curves. The third, given these Franck–Condon factors, the previously calculated relevant energies for the vibrational levels of the respective electronic states (relative to the $\nu'' = 0$ level of the ground electronic state) and the experimental energy-loss spectra, extracts the differential cross sections for each state. Each program can be run independently, or the three can run in sequence to determine these cross sections from the spectroscopic constants and the experimental energy-loss spectra. The application of these programs to the specific case of electron scattering from nitric oxide (NO) is demonstrated.

1. Introduction

Determination of low-energy ($\leq$100 eV) electron-impact excitation cross sections of molecules not only provides crucial information required in many natural phenomena but also provides the basis for developing a more complete understanding of electron collisions with complex targets (Takayanagi 1983; Kirby 1993). The energy-loss spectrum for this excitation (the intensity of the features in the energy-loss spectrum being proportional to the respective differential cross sections) is a complicated function, consisting of overlapping series of peaks corresponding to vibrational levels from one or more electronic states, all affected by the instrumental response function. These peaks (location and magnitude) can be approximately represented by the energies of the vibrational levels and the Franck–Condon factor for each level, modified by the instrumental response function.

As a first step in extracting electron collision parameters from electron energy-loss spectra, the potential-energy curves and Franck–Condon factors and

* Dedicated to Professor Robert W. Crompton on the occasion of his seventieth birthday.

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vibrational energies for the electronic states of diatomic molecules are determined. The differential cross section for each state can then be determined by 'fitting' the contribution of the vibrational levels of that state to the observed spectrum. In practice, this is difficult due to the superposition of many overlapping features in the spectrum, so that deconvolution is required. This can be done using a least-squares fitting technique first described by Trajmar *et al.* (1971). The fit can converge to an unphysical solution unless reasonable initial estimates are available. Nickel *et al.* (1989) found such estimates by identifying isolated features in the observed spectrum with a particular state and removing the contribution of that state, repeating these two steps until no recognisable features were left.

Three computer programs are reported here which allow the cross sections to be determined from spectroscopic data and independently measured energy-loss spectra. Two of the programs are enhanced versions of codes (Albritton *et al.* 1976, 1979) that have been used for many years to determine potential curves, energies of the vibrational levels of the relevant electronic states and Franck–Condon factors. The third is an independently written program which follows the method of Nickel *et al.* (1989) in finding the cross sections by a least-squares multiparameter fit to the experimental spectrum, but provides a range of methods to allow a mix of manual and automatic selection of the *ab initio* estimates. The current least-squares fitting code also incorporates a procedure, based on Bevington and Robinson (1992), which enables determination of numerically valid confidence limits on the parameters derived from the fit.

2. Theory

(2a) Potential Energy Curves

One of the most practical, and accurate, methods for generating potential energy (PE) curves is the Rydberg–Klein–Rees (RKR) procedure (Rydberg 1931; Klein 1932; Rees 1947). The RKR code provided here is basically that originally described by Albritton *et al.* (1979) which has been used extensively for many years to treat a very large number of diatomic molecular states. This code generates PE curves from the customary vibrational and rotational constants (i.e. Dunham expansion coefficients),

$$G_\nu = \omega_e \left(\nu + \tfrac{1}{2}\right) - \omega_e x_e \left(\nu + \tfrac{1}{2}\right)^2 + \omega_e y_e \left(\nu + \tfrac{1}{2}\right)^3 + \omega_e z_e \left(\nu + \tfrac{1}{2}\right)^4 + \dots, \quad (1)$$

where G_ν is the vibrational energy term (value in cm^{-1} and related to the energy E_ν for vibrational quantum number ν by $G_\nu = E_\nu/hc$), ω_e, $\omega_e x_e$, $\omega_e y_e$ and $\omega_e z_e$ are harmonic and anharmonic vibrational spectroscopic constants, and

$$B_\nu = B_e - \alpha_e \left(\nu + \tfrac{1}{2}\right) + \gamma_e \left(\nu + \tfrac{1}{2}\right)^2 \dots, \quad (2)$$

where B_ν is the rotational constant for vibrational level ν (Herzberg 1950, pp. 92, 106). These spectroscopic constants are defined and collected in the classic works by Herzberg (1950) and Huber and Herzberg (1979) and are frequently obtained by weighted least-squares fits (Albritton *et al.* 1976) to band origin and rotational constant data obtained from high-resolution optical photoelectron spectroscopy.

A detailed discussion of the RKR formulation, and its numerical implementation, was given by Zare (1964). The potential function V is obtained by connecting the turning points R_+ and R_- with a smooth curve by interpolation, with the turning points for a vibrational level of energy E_ν being given by

$$R_\pm(E_\nu) = \left[\frac{f(E_\nu)}{g(E_\nu)} + f^2(E_\nu)\right]^{\frac{1}{2}} \pm f(E_\nu)\,, \tag{3}$$

where $f(E_\nu)$ and $g(E_\nu)$ are found by evaluation of

$$f(E_\nu) = \frac{h}{2\pi(2\mu)^{\frac{1}{2}}} \int_0^{I'} [E_\nu - E(I,\kappa)]^{-\frac{1}{2}}\, dI\,, \tag{4}$$

$$g(E_\nu) = \frac{h}{2\pi(2\mu)^{\frac{1}{2}}} \int_0^{I'} \frac{\partial hc\,(G_I + B_I)}{\partial\kappa} [E_\nu - E(I,\kappa)]^{-\frac{1}{2}}\, dI\,, \tag{5}$$

where $E(I,\kappa)$ is the sum of vibrational and rotational energies up to E_ν (for which $I = I'$),

$$I = h\left(\nu + \tfrac{1}{2}\right), \text{ and } \kappa = \frac{J(J+1)h^2}{8\pi^2\mu}\,,$$

where μ is the reduced mass and h is Planck's constant.

A summary of the numerical techniques used to evaluate these integrals is given by Zare (1964) and is the one used in the RKR program reported here.

(2b) Franck–Condon Factors

The Franck–Condon factors are obtained from the definition

$$q_{\nu'\nu''} \equiv \int \Psi_{\nu'J'}(R)\Psi_{\nu''J''}(R)dR\,, \tag{6}$$

where $\Psi_{\nu'J'}$ ($\Psi_{\nu''J''}$) is the vibrational wavefunction for the final (initial) electronic state and the integration is over the internuclear distance R. (The customary notation of double-primes for the initial state, and single-primes for the final state, is used here). The vibrational wavefunctions are obtained by solving the radial Schrödinger equation (Zare 1964; Albritton *et al.* 1976)

$$\frac{d^2}{dR^2}\Psi_{\nu J} + [E_{\nu J} - U(R,J)]\Psi_{\nu J} = 0\,, \tag{7}$$

where $U(R,J)$ is the 'effective' radial potential energy for the initial or final electronic state, and $E_{\nu J}$, the energy eigenvalues of (7), represent the energies of the vibrational levels of a given electronic state. Note that length is measured in Bohr radii a_0 and the unit of energy is $hN_0/8\pi^2 c a_0^2\mu = 0\cdot948844$ cm^{-1}, where N_0 is Avogadro's number (physical scale) and μ is the reduced mass in Aston units (Herzberg 1950).

The 'effective' radial potential energy is defined (Zare 1964) according to

$$U(R,J) = V(R) + B_\nu[J(J+1)]\,, \tag{8}$$

where the rotational constant for a specific vibrational level B_ν is related to the rotational spectroscopic constants by (2) above. The spectroscopic 'term value' for a (ν, J) rovibrational level is then given by (Herzberg 1950, pp. 106–7)

$$T(\mathrm{cm}^{-1}) = G_\nu + F_\nu(J)\ , \tag{9}$$

with

$$F_\nu(J) = B_\nu J(J+1) - D_\nu J^2(J+1)^2\,,$$

where D_ν is the mean rotational constant representing the influence of centrifugal force.

Note that the only dependence of the vibrational energies, and associated wavefunctions, on the rotational quantum number J is contained explicitly in (8). In those applications for which transitions between specific rotational levels are not of interest, one can set $J = 0$ which results in a complete separation of the rotational and vibrational motion in the diatomic molecule.

(2c) Differential Cross Sections

The differential cross section $DCS(E_0, \theta_e)$ relates the scattered intensity dN to the incident electron beam current I_0, the target beam density ρ, an instrumental factor C and an annular differential increment of solid angle $d\Omega$:

$$dN = DCS(E_0, \theta_e) I_0 \rho C d\Omega \tag{10}$$

for impact energy E_0 at scattering angle θ_e.

Based on the assumptions (Brunger and Teubner 1990) that:

- the contribution of any one vibrational level is spread out (due to the experimental resolution) as a Gaussian distribution, i.e. the experimental resolution function F is approximated by:

$$F(W_{n'\nu'} - W) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(W_{n'\nu'} - W)^2}{2\sigma^2}\right), \tag{11}$$

  where $W_{n'\nu'}$ is the excitation energy for vibrational level ν' of electronic state n', W is the energy loss and $2\cdot 35\sigma$ is the full width at half maximum of this resolution function;
- the width of the rotational energy distribution in the ground vibrational level and final vibrational level can be neglected compared with the width of the experimental resolution function; and
- the relative vibrational energies are independent of the incident energy and scattering angle;

the scattered intensity $S(E_0, \theta_e, W)$ is given by

$$S(E_0, \theta_e, W) = \sum_{n'=0}^{N} X_{n'}(E_0, \theta_e) \sum_{\nu'=0}^{M(n')} q_{\nu'\nu''} F(W_{n'\nu'} - W) + B(W)\,, \qquad (12)$$

where

$$X_{n'}(E_0, \theta_e) = I_0 \rho C(E_0, \theta_e) DCS(E_0, \theta_e)_{n'}$$

and where $q_{\nu'\nu''}$ is the Franck–Condon factor (at excitation energy $W_{n'\nu'}$), $M(n')$ is the number of vibrational bands within state n', N is the number of electronic states, $B(W)$ is any background present, $DCS(E_0, \theta_e)_{n'}$ is the differential cross section for electronic state n' and $C(E_0, \theta_e)$ incorporates any other instrumental factors.

3. Computational Form of the Approximations

(3a) Franck–Condon Factors

The eigenvalue equation (7) is solved by iteration using the Cashion–Cooley (Cashion 1963; Cooley 1961) method which is based on an even-interval Numerov method of integration (Zare 1964). Since the vibrational wavefunctions have been determined on an even-interval grid, Simpson's rule integration is used for determining the Franck–Condon (FC) factors from equation (6).

The RKR program provides the potential energy curve for a given electronic state at the classical turning points of each of the vibrational levels (two for each level). In order to solve (7), the RKR potential is interpolated over the evenly-spaced mesh provided as input to the FC program and extrapolated (if required) outside the data range provided according to

$$V(R) = \frac{a}{R^{12}} + b \qquad \text{[repulsive wall at small } R\text{]},$$

$$V(R) = \frac{a'}{R^{b'}} \qquad \text{[asymptotic dependence at large } R\text{]},$$

where the pairs of constants (a, b) and (a', b') are determined by fitting to the last two pairs of points at both small and large R provided by the RKR program.

Table 1 provides a comparison of the measured and calculated vibrational energy levels and rotational constants for the ground state of NO. The two columns labelled 'poly. fit RKR' contain the rotationless vibrational levels and rotational constants calculated in the RKR program from spectroscopic constants (Huber and Herzberg 1979) using the polynomial expansions given in (1) and (2), respectively. Comparing these two columns with the corresponding columns labelled 'measured' provides an indication of the ability of the polynomial expansion to fit the measured vibrational and rotational energy-level data over the range of vibrational levels from 0 to 19 in the NO ground state. The first of the two columns labelled 'calculated FC pgm' contains the vibrational energy levels obtained as eigenvalues of the Schrödinger equation (7), using the RKR potential ($J = 0$). The accuracy (relative to the column labelled 'measured') of these

Table 1. Comparison of measured and calculated spectral properties for NO [$X^2\Pi$]

	$G(\nu)$[cm^{-1}]				$B(\nu)$[cm^{-1}]			
ν''	Measured[A]	Poly. fit RKR	Calculated FC pgm	Difference [meas.−calc.]	Measured[A]	Poly. fit RKR	Calculated FC pgm	Difference [meas.−calc.]
0	948·66	948·66	948·679	−0·019	1·69562	1·69562	1·69562	0·00000
1	2824·76	2824·76	2824·820	−0·060	1·6783[B]	1·67827	1·67826	0·00004
2	4672·68	4672·68	4672·769	−0·089	1·6608[B]	1·66084	1·66083	−0·00003
3	6492·51	6492·52	6492·624	−0·114	1·6433[B]	1·64334	1·64333	−0·00003
4	8284·34	8284·34	8284·463	−0·123	1·62624	1·62576	1·62575	0·00049
5	10048·21	10048·21	10048·342	−0·132	1·60782	1·60811	1·60810	−0·00028
6	11784·15	11784·16	11784·287	−0·137	1·59040	1·59039	1·59038	0·00002
7	13492·19	13492·20	13492·309	−0·119	1·57227	1·57259	1·57259	−0·00032
8	15172·30	15172·32	15172·392	−0·062	1·55452	1·55472	1·55473	−0·00021
9	16824·45	16824·47	16824·502	−0·052	1·53657	1·53677	1·53679	−0·00022
10	18448·58	18448·61	18448·615	−0·035	1·51798	1·51875	1·51879	−0·00081
11	20044·62	20044·66	20044·661	−0·041	1·49987	1·50066	1·50071	−0·00084
12	21612·45	21612·51	21612·514	−0·064	1·48412	1·48249	1·48255	−0·00157
13	23151·97	23152·05	23152·046	−0·076	1·4641[C]	1·4642	1·46432	−0·00022
14	24663·02	24663·11	24663·112	−0·092	1·4455[C]	1·4459	1·44600	−0·00050
15	26145·43	26145·54	26145·544	−0·114	1·4273[C]	1·4275	1·42758	−0·00028
16	27599·01	27599·15	27599·151	−0·141	1·4085[C]	1·4091	1·40905	−0·00055
17	29023·55	29023·72	29023·720	−0·170	—	1·39054	1·39037	—
18	30418·81	30419·02	30419·015	−0·205	—	1·37193	1·37149	—
19	31784·54	31784·28	31784·779	−0·239	—	1·35324	1·35224	—

[A] Engleman *et al.* (1970).
[B] Interpolated.
[C] Lagerquist and Miescher (1958).

calculated vibrational energies is determined by both the numerical accuracy of the algorithms used to solve (7) and the validity of the approximations used to derive (7) itself (e.g. the Born–Oppenheimer separation of nuclear and electronic motion, see Herzberg 1950; Zare 1964). This is clearly also very important in determining the accuracy of the calculated Franck–Condon factors, as obtained from equation (6). The sensitivity of the absolute value of the eigenvalues of (7) to the mesh size was tested by doubling the number of mesh points (from 2000 to 4000 points) and it was found that 2000 points is generally sufficient except for the very broad (i.e. $R_{max} - R_{min} \geq 0{\cdot}6$ Å) potential energy curves occasionally encountered.

The second column labelled 'calculated FC pgm' enables a comparison of the measured and calculated rotational constants for each vibrational level in the NO ground state. The rotational constant for each vibrational level is proportional to the reciprocal moment of inertia and is calculated according to (Herzberg 1950, p. 106)

$$B_\nu = \frac{h}{8\pi^2}\left\langle \frac{1}{R^2} \right\rangle \ , \tag{13}$$

where the brackets in (13) denote the mean value of $1/R^2$ for the particular vibrational level.

Although we have not conducted an exhaustive study of diatomic molecules, the results in Table 1 suggest that the combination of the RKR and FC programs can probably be expected to produce results accurate to $0{\cdot}1$–$0{\cdot}2$ cm^{-1}, for the vibrational energy levels, and to $0{\cdot}0003$–$0{\cdot}0010$ cm^{-1}, for the rotational

constants, for diatomic molecules (other than H_2 and He_2) and vibrational levels which are not strongly perturbed.

(3b) Determination of Differential Cross Sections

Given an experimental energy-loss spectrum $y(W)$, the coefficients $X_{n'}(E_0, \theta_e)$ are determined by a multiparameter fit of the predicted intensity $S(E_0, \theta_e, W)$, as defined in (12), to the observed spectrum. The background is approximated by the quadratic function

$$B(W) = \sum_{i=1}^{3} a_i W^{i-1} . \tag{14}$$

As $I_0 \rho C(E_0, \theta_e)$ is constant for a particular spectrum, relative values of the differential cross section $DCS(E_0, \theta_e)_{n'}$ are determined by a least squares fit of $S(E_0, \theta_e, W)$ to the observed spectrum, with the values of $X_{n'}(E_0, \theta_e)$, σ and a_i being varied. To allow for any systematic error in the energy-loss scale measurement, the position of the 'zero channel' which specifies 0 eV energy loss (i.e. the position of the elastic peak) is also a variable parameter in the fit.

This multiparameter fitting is implemented using the Marquardt method of least-squares fitting described by Bevington and Robinson (1992). This minimises the value of χ^2 and χ^2_ν in

$$\chi^2 = \sum_{k=1}^{K} \frac{[y(W_k) - S(E_0, \theta_e, W_k)]^2}{y(W_k)} \qquad \text{and} \qquad \chi^2_\nu = \frac{\chi^2}{K - k_c} , \tag{15}$$

where k_c is the number of variable parameters. This gives a large weighting to small values of $y(W_k)$, which may result in too much emphasis being placed on the fitting to insignificant features, so an alternative with equal weighting of data points is provided by

$$\chi'^2 = \frac{\sum_{k=1}^{K} [y(W_k) - S(E_0, \theta_e, W_k)]^2}{K - k_c} .$$

The errors in each of the fitted parameters are determined by a method of Bevington and Robinson (1992). One parameter is varied, keeping the other $(k_c - 1)$ parameters fixed, until a case is found where χ^2_ν has changed by $1 \cdot 0$ from the minimum given by (15). The corresponding change in the parameter is one standard deviation.

The fitting procedure requires initial estimates of the parameters which are to be varied, both to allow it to iterate and to ensure that the fit does not converge to a local minimum. Nickel *et al.* (1989) found initial estimates by repeatedly choosing a particular state for which isolated features in the spectrum could be identified, scaling its contribution to match these features, and subtracting out its contribution. The scaling factors were then used as the initial estimates.

In this implementation a less rigorous method is used to find the initial estimates, to accommodate the fit when it is working with data exhibiting more

scatter. The initial estimate of σ is made from the autocorrelation function of the data. The initial estimates for the relative cross sections and background constants are based on the limitation that any one contributor cannot have an intensity anywhere in the spectrum that is larger than the experimental value, i.e.

$$X_{n'}(E_0, \theta_e) = \min\left\{\frac{y(W_k)}{\Sigma_{\nu'=0}^{M(n')} q_{\nu'\nu''} F(W_{n'\nu'} - W_k)}, k = [1, K]\right\}, \tag{16}$$

$$a_i = \min\left\{\frac{y(W_k)}{W_k^{i-1}}, k = [1, K]\right\} \ . \tag{17}$$

To deal with exceptional cases in which these initial estimates are not sufficiently close to the actual values, two other facilities are provided:

- A 'trial-and-error' fitting procedure can be run to provide initial estimates for the 'least-squares' procedure. For each component in turn, a range of different values of the fitting parameters are tried to minimise χ^2. The trial values have a random component to avoid the search getting stuck on a local minimum. This technique is useful if there is substantial noise in the measurements.
- The ability to set particular initial estimates, or to restrict particular coefficients to a constant value or an allowed range.

4. Program Description

The RKR and FC codes provided here are modified versions of the codes originally written by Zare (1964) and by Albritton *et al.* (1979). Both codes have been extensively edited to incorporate detailed instructions for their use in comment cards at the beginning of them, which we do not detail further here. We note that both the RKR and FC codes have also been modified from their original forms to be compatible with FORTRAN 77.

The RKR code finds the transition energies for a diatomic molecule using the Rydberg–Klein–Rees method. The user must specify in an input file the masses of the atoms, and the spectroscopic constants which define G_ν and B_ν (as in equations 1 and 2). The FC code reads a potential curve from a file, interpolates to a desired spacing and computes the intensity distribution of electronic transitions, using the radial Schrödinger (7) and Simpson's rule, thus finding the FC factors.

An additional program *'rkrfcf'* is provided to convert output from the RKR code to input for the FC code. On rare occasions the FC code fails to do the integration and, under this circumstance, the input file must be edited to judiciously select a better range of integration. The input file produced by *'rkrfcf'* is annotated to make this editing easier.

A program *'fitcomp'* finds a set of coefficients $X_{n'}(E_0, \theta_e)$, given the FC factors with the transition energies and the experimental spectrum of intensity against energy-loss. The absolute excited electronic-state differential cross sections can be determined from this set if the elastic peak is included in the spectrum (Brunger and Teubner 1990), by calculating (in turn) the ratio of the coefficients for the electronic channel of interest to the elastic channel and then multiplying this

ratio by the known absolute elastic differential cross section. This elastic cross section is usually determined in a separate series of experiments based on the relative flow technique (Nickel *et al.* 1989; Mojarrabi *et al.* 1995).

Program *'fitcomp'* is written in FORTRAN 77 with some common extensions. It takes as input the FC factors and vibrational energy levels (as produced by the FC code) and an experimental energy-loss spectrum. It computes the coefficients which give the best fit of the computed spectrum to the observed spectrum. It allows the user to eliminate particular states or background components, or to constrain particular coefficients to set values or ranges.

These choices and other parameters must be entered when the program is run. These are explained in 'on-line' documentation. When run interactively, these parameters are written to a file which can then be used for running in batch mode.

The program is preloaded with a set of energies and FC factors for a fit to nitric oxide (Mojarrabi *et al.* 1996). They can be replaced, for NO or other molecules, with different electronic states, energies and factors by input files in the same format as the output of the FC code. Program *'fitcomp'* produces output files as described below:

- *MoEoBo_modl_bck.fit* This lists the experimental spectrum and the fitted spectrum, plus a comparison spectrum if requested, for molecule *Mo*, impact energy *Eo* and scattering angle *Bo*, using model *modl* with background (none, constant, linear or quadratic) *bak*.
- *MoEoBo_modl_bck.com* This lists the contribution to the spectrum for each component state.
- *MoEoBo_modl_bck.cof* This lists the coefficients for each state which give the best least-squares fit, along with the error calculated by the least-squares procedure.
- *MoEoBo_modl_bck.err* This gives a list of the coefficients and true errors, determined using the method of Bevington and Robinson (1992).

A program *'plotcomp'* is included to produce Tektronix-4014 or Postscript plots of these output files. It will plot either or both of the spectra listed in the *'.fit'* file and the individual components of the fitted spectrum from the *'.com'* file. For the first option it also plots the difference, $y(W_k) - S(E_0, \theta_e, W_k)\ \forall k$, between the experimental and fitted intensities at each value of energy loss, providing an alternative means to assess the overall quality of the fit and to identify where, in energy loss, the fit to the data is poorest.

5. Sample Inputs and Corresponding Outputs

A fit produced by this suite of programs is shown in Fig. 1*a*. The discrete error bars indicate an energy-loss spectrum measured by Mojarrabi *et al.* (1996). The curve indicates the fit determined by running the suite of programs *'rkr', 'rkrfcf', 'fcf'* and *'fitcomp'* and then plotting the contents of the output file *'no3090_fcfv_qad.fit'* using program *'plotcomp'*. The difference between the experimental and fitted intensities is shown in Fig. 1*b*.

The fit to the data in Fig. 1 is not perfect, reflecting, amongst other things, the strong Rydberg-valence perturbations in the NO molecule for states with energy loss above $6 \cdot 7$ eV. Procedures for dealing with this are beyond the scope

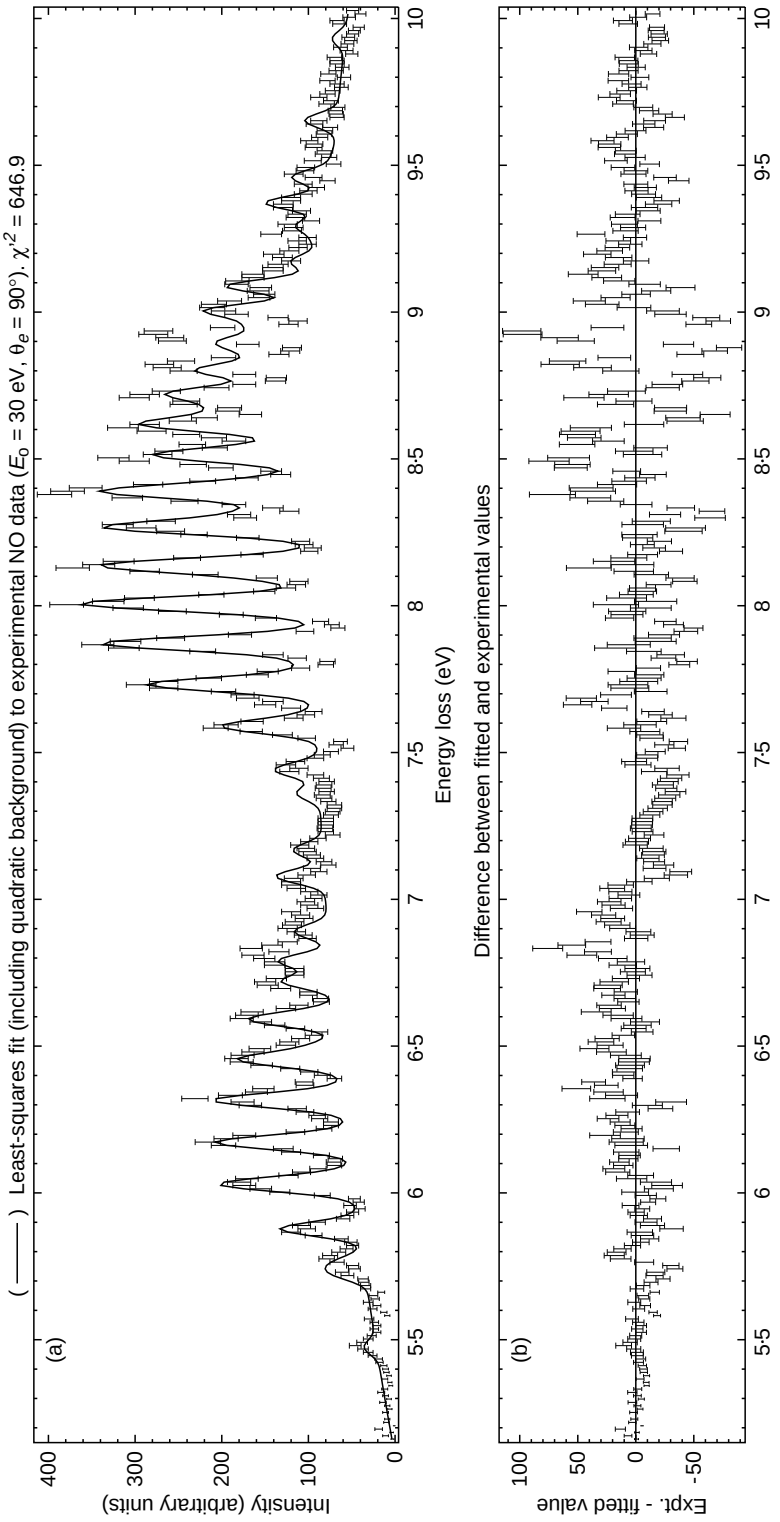

Fig. 1. (*a*) Electron energy-loss spectrum for e^-+NO scattering at $E_0 = 30$ eV and $\theta_e = 90°$. The data of Mojarrabi *et al.* (1996) (I) and the fit to those data, using the energies and FC factors produced by '*fcf*' (—) are depicted. (*b*) Difference spectrum plot between the fitted and experimental intensities (I), at each value of energy loss, for the energy-loss spectrum in (*a*) above. See text for further details.

Table 2. Excitation energies ($E_{\nu'0}$) and Franck–Condon factors ($q_{\nu'0}$) for transitions from $X^2\Pi(\nu''=0)$ to the indicated final state of NO, as derived using *'fcf'*

$a^4\Pi$		$C^2\Pi(3p\pi)$		$B'^2\ \Delta$		$H^2\Sigma^+(3d\sigma)$		$Q^2\Pi\ (5p\pi)$	
$E_{\nu'0}$	$q_{\nu'0}$	$E_{\nu'0}$	$q_{\nu'0}$	$E_{\nu'0}$	$q_{\nu'0}$	$E_{\nu'0}$	$q_{\nu'0}$	$E_{\nu'0}$	$q_{\nu'0}$
4·745	0·0000	6·499	0·1444	7·442	0·0199	7·773	0·1517	8·515	0·1342
4·868	0·0001	6·790	0·3399	7·589	0·0630	8·063	0·3173	8·802	0·2724
4·989	0·0004	7·078	0·3183	7·732	0·1102	8·353	0·2924	9·088	0·2713
5·107	0·0012	7·361	0·1519	7·871	0·1412	8·643	0·1596	9·372	0·1793
5·222	0·0027	7·641	0·0395	8·007	0·1484	8·933	0·0590	9·653	0·0895
5·335	0·0051	7·917	0·0056	8·138	0·1361	9·223	0·0161	9·932	0·0362
5·445	0·0087	8·189	0·0004	8·266	0·1128			10·209	0·0124
5·551	0·0132			8·390	0·0866	$H'^2\Pi(3d\pi)$		10·484	0·0037
5·654	0·0183	$L'^2\Phi$		8·510	0·0627	$E_{\nu'0}$	$q_{\nu'0}$		
5·754	0·0238	$E_{\nu'0}$	$q_{\nu'0}$	8·626	0·0432	7·806	0·1351	$T^2\Sigma^+(6s\sigma)$	
5·851	0·0290	6·599	0·0000	8·738	0·0287	8·096	0·3101	$E_{\nu'0}$	$q_{\nu'0}$
		6·721	0·0001	8·847	0·0184	8·382	0·3069	8·674	0·0863
$A^2\Sigma^+(3s\sigma)$		6·840	0·0004			8·664	0·1719	8·964	0·2189
$E_{\nu'0}$	$q_{\nu'0}$	6·956	0·0010	$E^2\Sigma^+(4s\sigma)$		8·942	0·0602	9·251	0·2806
5·473	0·1628	7·070	0·0023	$E_{\nu'0}$	$q_{\nu'0}$	9·216	0·0137		
5·763	0·3349	7·181	0·0044	7·546	0·1822			$U^2\Delta(5d\delta)$	
6·050	0·2935	7·290	0·0074	7·837	0·3438	$K^2\Pi(4p\pi)$		$E_{\nu'0}$	$q_{\nu'0}$
6·332	0·1484	7·397	0·0113	8·123	0·2859	$E_{\nu'0}$	$q_{\nu'0}$	8·705	0·0864
6·610	0·0481	7·501	0·0158	8·405	0·1387	7·977	0·1369	8·995	0·2193
6·884	0·0105	7·602	0·0208			8·267	0·3842	9·281	0·2811
7·154	0·0016	7·701	0·0258	$F^2\Delta$		8·545	0·3522		
		7·798	0·0305	$E_{\nu'0}$	$q_{\nu'0}$	8·812	0·1166	5f	
$b^4\Sigma^-$		7·892	0·0348	7·692	0·1957	9·066	0·0100	$E_{\nu'0}$	$q_{\nu'0}$
$E_{\nu'0}$	$q_{\nu'0}$	7·983	0·0384	7·984	0·3613	9·308	0·0000	8·718	0·1593
5·725	0·0361	8·072	0·0412	8·271	0·2835			9·009	0·2957
5·877	0·0991	8·159	0·0431	8·553	0·1225	$M^2\Sigma^+(4p\sigma)$		9·295	0·2802
6·027	0·1502	8·243	0·0442	8·830	0·0316	$E_{\nu'0}$	$q_{\nu'0}$		
6·172	0·1671	8·324	0·0446	9·102	0·0049	8·017	0·1235	$W^2\Pi(6p\pi)$	
6·314	0·1533	8·403	0·0443			8·304	0·2960	$E_{\nu'0}$	$q_{\nu'0}$
6·453	0·1236	8·479	0·0435	$G^2\Sigma^-$		8·586	0·3175	8·772	0·1593
6·588	0·0910	8·553	0·0422	$E_{\nu'0}$	$q_{\nu'0}$			9·062	0·2956
6·720	0·0629	8·625	0·0405	7·750	0·0025	$S^2\Sigma^+(5s\sigma)$		9·349	0·2800
		8·694	0·0386	7·881	0·0115	$E_{\nu'0}$	$q_{\nu'0}$		
$B^2\Pi_r$		8·760	0·0365	8·011	0·0281	8·324	0·1968	$Y^2\Sigma^+(6p\sigma)$	
$E_{\nu'0}$	$q_{\nu'0}$	8·824	0·0342	8·137	0·0493	8·615	0·3572	$E_{\nu'0}$	$q_{\nu'0}$
5·642	0·0000	8·886	0·0319			8·901	0·2868	8·784	0·0343
5·769	0·0001	8·944	0·0296	$L^2\Pi$				9·074	0·1238
5·894	0·0006	9·001	0·0273	$E_{\nu'0}$	$q_{\nu'0}$	$N^2\Delta$		9·361	0·2258
6·018	0·0017	9·055	0·0252	7·751	0·0000	$E_{\nu'0}$	$q_{\nu'0}$		
6·139	0·0039	9·106	0·0235	7·866	0·0002	8·383	0·2287	$Z^2\Sigma^+(7s\sigma)$	
6·259	0·0075	9·155	0·0229	7·979	0·0006	8·673	0·3836	$E_{\nu'0}$	$q_{\nu'0}$
6·376	0·0129			8·088	0·0014	8·960	0·2656	8·860	0·2693
6·491	0·0198	$D^2\Sigma^+(3p\sigma)$		8·195	0·0027	9·244	0·0983	9·151	0·3490
6·605	0·0280	$E_{\nu'0}$	$q_{\nu'0}$	8·299	0·0046	9·523	0·0211	9·437	0·2363
6·715	0·0368	6·607	0·1600	8·400	0·0068				
6·824	0·0456	6·890	0·3398	8·499	0·0093	$O'^2\Pi+O^2\Sigma^+$		6dδ	
6·930	0·0538	7·167	0·3035	8·595	0·0119	$E_{\nu'0}$	$q_{\nu'0}$	$E_{\nu'0}$	$q_{\nu'0}$
7·033	0·0607	7·438	0·1474	8·687	0·0143	8·430	0·1625	8·876	0·5247
7·134	0·0660	7·703	0·0419	8·777	0·0164	8·720	0·3321	9·167	0·3225
7·231	0·0695	7·963	0·0069	8·865	0·0182	9·006	0·3029	9·453	0·1164
7·326	0·0711			8·949	0·0197				
7·418	0·0708							6f	
7·506	0·0688							$E_{\nu'0}$	$q_{\nu'0}$
7·590	0·0653							8·885	0·0862
7·671	0·0606							9·176	0·2186
7·748	0·0548							9·462	0·2805
7·820	0·0482								
7·888	0·0410								
7·951	0·0336								
8·010	0·0262								
8·063	0·0191								
8·110	0·0129								
8·152	0·0079								

of this paper but have been discussed previously by Nickel *et al.* (1989) and more recently by Brunger and Buckman (1997).

To enable the fit embodied in Fig. 1*a* to be reproduced, spectroscopic components are given in file *'rkr.input'*, dissociation energies in *'rkrfcf.dat'*, the experimental energy-loss spectrum in *'no3090.dat'* and the input parameters for *'fitcomp'* in *'fitcomp.bat'*. A Unix script file *'test_no3090'* runs *'rkr'*, *'rkrfcf'*, *'fcf'* and *'fitcomp'* in sequence. For non-Unix users, the sequence of operations which it performs is:

- Copy the file *'rkr.input'* to *'tape5'*
- Compile and execute *'rkr.f'*
- Compile and execute *'rkrfcf.f'*
- Compile and execute *'fcf.f'*
- Rename file *'tape7'* to *'no.fcfv'*
- Compile and execute *'fitcomp.f'*, choosing the *'fcfv'* model.

The vibrational energy levels and associated FC factors produced by the RKR and FC procedures (in *'tape7'*) are reproduced in Table 2. The validity of all the output files produced by *'fitcomp'* may be checked by comparing the files *'no·3090_fcfv_qad.*'* with those labelled *'sample.*'* that are supplied with the programs.

6. Summary

A suite of programs is described which, given spectroscopic constants and experimental energy-loss spectra for electron-impact excitation of a given molecule, allows the determination of absolute differential cross sections for each electronic state of that molecule. The RKR code calculates potential curves from spectroscopic components. The FC code then calculates the vibrational energy levels and Franck–Condon factors. Given these levels and factors, *'fitcomp'* fits a predicted spectrum to an experimental one, finding relative electronic state differential cross sections. The absolute differential cross sections can then be determined, if the elastic peak is included in the spectrum, by calculating (in turn) the ratio of the coefficients for the electronic channel of interest to the elastic channel and then multiplying this ratio by the known absolute elastic differential cross section. This elastic cross section is usually determined in a separate series of experiments based on the relative flow technique (Nickel *et al.* 1989; Mojarrabi *et al.* 1995).

The suite of programs and sample files can be obtained by electronic mail by contacting *phmjb@cc.flinders.edu.au*. As delivered, the programs should run and provide a fit for the $E_0 = 30$ eV and $\theta_e = 90^0$ energy-loss spectrum of NO.

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