

AUTOMATIC BACKGROUND SUBTRACTION IN GAS ELECTRON DIFFRACTION:
THE COVARIANCE MATRIX IN LEAST-SQUARES STRUCTURE-PARAMETER
ANALYSIS

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A new criterion is proposed for deriving the background by means of Tikhonov regularization. A software system has been written for complete and continuous automatic molecular-structure interpretation. The covariance matrix for $sM(s)$ has been calculated from 35 independent interpretations for the $HgBr_2$ molecule. Least-squares fitting has given the structural parameters of this molecule on the basis of the complete weighting matrix. Structural data are also presented for $SbCl_3$ and $CsAlF_4$ derived by automatic processing.

At present, every laboratory employing gas electron diffraction has its software for processing data in stages. It has become important to provide complete and continuous automation in all processing stages; the more so because one of the key laborious operations is isolating and subtracting a background line, which is performed graphically. Clearly, complete automation provides the following: a) a substantial improvement in speed in measuring molecular parameters, b) improved reliability, and c) elimination of the subjective element. It is virtually impossible to calculate the background function theoretically because it is difficult to incorporate all the factors that influence it, and also because the contributions are random (inelastic molecular and multiple scattering, the finite volume of the scattering region, electron scattering at parts of the apparatus and at residual-gas molecules, errors in the sector function, errors in normalizing the experimental curves, etc.). Therefore, the practical implementation of any method of isolating the background gives only some approximation \tilde{I}_b , which will differ from the exact function the less the more completely one used the a priori information and the more correct the criterion for isolating it.

CRITERION FOR ISOLATING A SMOOTH BACKGROUND

Let $u^*(x)$ be an unknown function to be recovered. This may be the initial background distribution $I_b^0(s)$ or the background line correction function $\Delta(sM(s))$. Experiment gives a discrete set of points $u_\delta(x_i)$, which are related to $u^*(x_i)$ by

$$|u^*(x_i) - u_\delta(x_i)| \leq \delta_i. \quad (*)$$

One assumes that the δ_i are known with adequate accuracy. If u^* corresponds to I_b^0 , then $u_\delta(x_i) = I_{LEV}(x_i)$, or if u^* is $\Delta(sM(s))$, then $u_\delta(x_i) = \Delta(s_iM(s_i))$.

We determine the features of u^* :

- 1) $u^*(x)$ is continuously differentiable up to any order;
- 2) $u^*(x)$ has a small value for the curvature function:

$$h(u) = |u''|/(1 + u'^2)^{3/2}. \quad (**)$$

Our task is to use quantitative a priori information (*) and qualitative (**) information to recover the smooth function $u^*(x)$ and its derivative $du^*(x)/dx$ while estimating the accuracy of the approximation.

In [1] it is shown that recovering a function and its derivative from experimental data is an ill-posed problem, and a deterministic Bayes approach is given based on Tikhonov's regularization method. For a given function $u_\delta(x)$, we define the set of functions $D_\delta = \{u \in C^\infty[a, b]; \|u_\delta(x) - u(x)\| \leq \delta$ (here and subsequently by the norm $\|\cdot\|$ we mean the Euclidean

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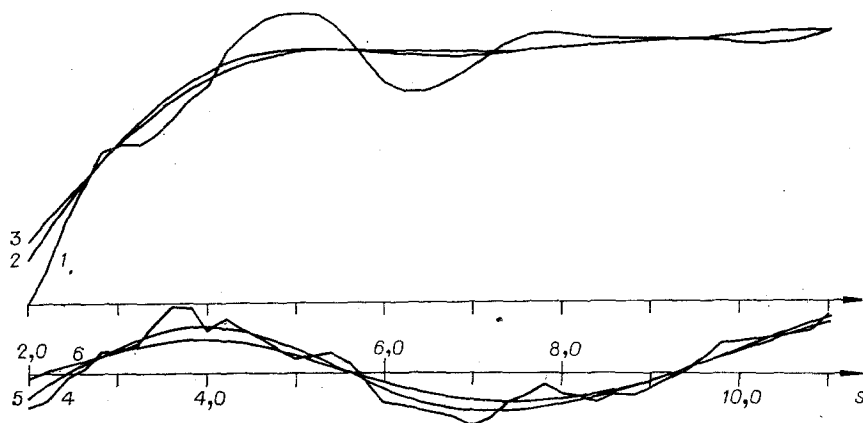


Fig. 1. 1) Smoothed intensity function I_{LEV} for $CsAlF_4$; 2) initial background line; 3) background line after correction; 4) $\Delta(sM(s)) = sI_{LEV}(s) - sI_b(s) - k \cdot sM(s)$; 5, 6) background line correction functions $\Delta(sM(s))$.

norm). As $\|k(u)\| \leq \|u''\|$, we introduce the following criterion for the function approximating u^* :

$$\inf \|u''\|, u \in D_\delta. \quad (1)$$

It is known that a solution of (1) exists and is unique (pp. 133-139 of [2]). The problem of (1) is reducible to the equivalent problem of unconditional minimization of the Tikhonov functional:

$$\inf \psi[u] = \|u - u_\delta\|^2 + \alpha \|u''\|^2, \quad (2)$$

where α is chosen from the condition $\|u_\alpha - u_\delta\| = \delta$, i.e., from the discrepancy (u_α is the solution to (2)) (p. 71 of [2]). Determining $\alpha = \alpha(\delta)$ requires considerable computation, so α is chosen from Tikhonov's classical rule: $\alpha = c\delta^2$, where the choice of c should be matched to the a priori information. We put $c = 1/R^2$, where $R = \|u_\delta''\|$. Then the choice of c provides an approximation of u_α to u^* better than when the regularization parameter is chosen from the discrepancy (pp. 194-202 of [3]). In [1] there are accuracy estimates and it is shown that the following conditions are obeyed: a) The solution exists, b) the solution is unique, and c) the solution is continuously dependent on the parameters.

DATA-PROCESSING LIBRARY FOR GAS ELECTRON DIFFRACTION

This criterion has been used in a software system for complete and continuous automatic processing of electron-diffraction patterns to determine molecular structures. We give the scheme for the head program operation:

1) The initial background line is chosen, taking $u^*(s) = I_b^0$. First, one constructs the cubic interpolation spline $u_\delta(s)$ from the known values $I_{LEV}(s_i)$:

- a) $u_\delta(s_i) = I_{LEV}(s_i)$;
- b) $u_\delta(s) = a_i s^3 + b_i s^2 + c_i s + d_i, s \in [s_i, s_{i+1}]$;
- c) $u_\delta(s) \in C^2[s_{\min}, s_{\max}]$;
- d) $u_\delta''(s_{\min}) = u_\delta''(s_{\max}) = 0$.

Then one calculates $R_2 = \|u_\delta''(s)\|^2$ from $R_0^2 = \sum_{i=1}^{N-1} 4h_i(3a_i^2 h_i^2 + 3a_i b_i h_i + b_i^2)$; putting $\alpha_0 = \delta_0^2/R_0^2$,

we solve (2) to give $u_\alpha(s)$, which is the desired $I_b^0(s)$. Experience shows that the value of the R factor for the initial parameter values and the calculated initial background line is in the range 15-25%.

2) The least-squares definition of the structure parameters is handled.

3) The correlation relation for the parameters is analyzed and checks are made on the computation termination criteria.

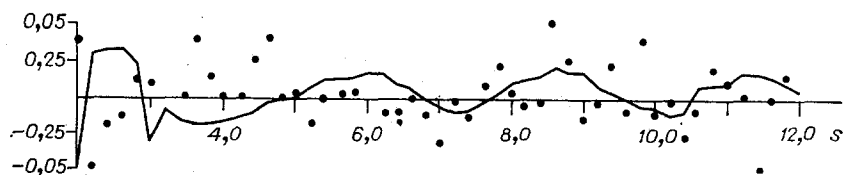


Fig. 2. The points denote the final values of $\Delta(s_i M(s_i))$ for SbCl_3 ; the solid line is $(s I_b^{\text{aut}} - s I_b^{\text{man}})$, where I_b^{man} is the final background function [5] (the error in determining the background does not exceed $\Delta(s M(s))$).

TABLE 1. Internuclear Distances r_α and Mean Nuclear Vibration Amplitudes l_m in SbCl_3 (error $3\sigma_{\text{LS}}$)

Distance	Our data, Å	Data of [5], Å
$r_\alpha(\text{Sb}-\text{Cl})$	$2,329 \pm 0,003$	$2,332 \pm 0,004$
$r_\alpha(\text{Cl} \dots \text{Cl})$	$3,506 \pm 0,015$	$3,497 \pm 0,015$
$l_m(\text{Sb}-\text{Cl})$	$0,051 \pm 0,012$	$0,057 \pm 0,012$
$l_m(\text{Cl} \dots \text{Cl})$	$0,126 \pm 0,016$	$0,123 \pm 0,019$

4) The background line is corrected, with the assumption

$$u^*(s) = \widetilde{\Delta(s M(s))}.$$

By analogy with point (1), a cubic interpolation spline is constructed from $\Delta(s_i M(s_i))$ and the solution to (2), $u_\alpha(s)$, is found for the calculated $\alpha_k = \delta_k^2 / R_k^2$. Then one corrects the background function: $I_b^{k+1} = I_b^k + u_\alpha(s)$ and goes to point 2).

After the primary processing (derivation of the mean ILEV), the time required to interpret a molecular structure is 10-30 min in interactive operation with an HP 21MX minicomputer (Hewlett Packard), or 3-5 min with the BESM-6, as has been found for the molecules CdCl_2 , CdBr_2 , HgBr_2 , SbCl_3 , CsAlCl_4 , CsAlF_4 , and so on. These molecules required 1-3 iterations in accordance with (2)-(4) [4]. This software system also provides the following: 1) noise filtration for the experimental ILEV (by regularization), 2) cubic interpolation spline construction on an uneven net, 3) distinguishing the background component in the oscillating function, 4) minimizing the quadratic functional subject to constraints of the form $x \geq 0$, $x \geq b$, $a \leq x \leq b$, $Ax \leq b$, 5) minimizing the discrepancy functional (R factor) with the complete weighting matrix, 6) performing a global minimization on many variables in a given direction, and 7) outputting the graphs to the printer and plotter.

STRUCTURAL STUDY OF SbCl_3 AND CsAlF_4 VIA THE AUTOMATED PROCEDURE

To check the methods, we made repeated structural studies on SbCl_3 and CsAlF_4 . In order to compare the final results (Tables 1 and 2), we took the initial data (ILEV(s), s_{min} , s_{max} , parameter values, etc.) from [5], where a complete structural study on SbCl_3 and CsAlF_4 was made with a graphical procedure for isolating the background (Figs. 1 and 2).

STATISTICAL DETERMINATION OF THE MEASUREMENT ERRORS FOR THE EXPERIMENTAL FUNCTION

In [6] it is claimed to be necessary to make a detailed evaluation of the errors at each stage in electron diffraction experiments. The main error sources in gas electron diffraction are familiar [8]. In accordance with the usual structure-analysis method, one normally employs the scattering intensity $I(s)$ obtained by averaging over several diffraction patterns. Here all the $I(s_i)$ are considered as equally accurate, which is incorrect in the general case [7]. Our purpose was an independent execution of numerous (about 40) experiments to provide statistical analysis of the $I_{\text{LEV}}(k)$, $I_b(k)$, $r_{\alpha ij}(k)$, $l_{mij}(k)$ data, where k is the experiment number. Mercury bromide was selected. The diffraction patterns were recorded with two distances L : 420 mm (20 experiments) and 660 mm (20 experiments). Tables 3 and 4 give the structural parameters for each experiment; in parentheses we give the $3\sigma_{\text{LS}}$ values. The data from certain

TABLE 2. Internuclear Distances r_a and Mean Nuclear Vibration Amplitudes l_m in CsAlF_4 (error $3\sigma_{\text{LS}}$)

Atoms	Our data		Data of [5]	
	$r_a, \text{Å}$	$l_m, \text{Å}$	$r_a, \text{Å}$	$l_m, \text{Å}$
Al—F	1,702(7)	0,06(3)	1,691(5)	0,06(1)
F ... F	2,74(3)	0,14(2)	2,70(5)	0,16(3)
Cs—F _δ	2,80(10)	0,30(7)	2,80(10)	0,25(8)
Cs—F _g	4,78(15)	0,42(12)	4,63(23)	0,43(15)
Cs—Al	3,51(7)	0,22(6)	3,56(11)	0,22(7)
R, %	8,73		13,77	

TABLE 3. Determining the Parameters of HgBr_2 with L = 420 mm

Expt. No.	R, %	$r_a(\text{Hg—Br}), \text{Å}$	$l_m(\text{Hg—Br}), \text{Å}$	$r_a(\text{Br—Br}), \text{Å}$	$l_m(\text{Br—Br}), \text{Å}$
1	13,0	2,382(6)	0,038(15)	4,376(30)	0,063(42)
2	11,3	2,382(4)	0,043(12)	4,736(33)	0,089(33)
3	10,9	2,381(4)	0,037(13)	4,746(36)	0,091(33)
4	11,4	2,386(5)	0,044(12)	4,765(33)	0,086(33)
5	15,2	2,385(6)	0,047(15)	4,772(42)	0,081(45)
6	12,5	2,386(5)	0,039(15)	4,731(27)	0,058(42)
7	12,3	2,382(5)	0,022(24)	4,756(42)	0,096(39)
8	14,4	2,385(6)	0,040(15)	4,739(33)	0,057(45)
9	12,4	2,378(5)	0,032(18)	4,732(48)	0,108(42)
10	14,1	2,387(6)	0,036(18)	4,745(30)	0,046(48)
11	12,1	2,382(5)	0,036(15)	4,747(33)	0,080(36)
12	12,0	2,384(5)	0,027(18)	4,744(30)	0,066(36)
13	11,1	2,379(4)	0,028(18)	4,755(33)	0,090(36)
14	15,6	2,385(6)	0,032(23)	4,745(51)	0,096(51)
15	13,6	2,382(6)	0,044(15)	4,754(36)	0,072(42)
16	13,1	2,385(6)	0,043(15)	4,726(36)	0,086(42)
17	11,8	2,384(5)	0,041(12)	4,756(30)	0,073(33)
18	12,0	2,378(5)	0,042(12)	4,729(30)	0,074(36)
Mean		2,383	0,037	4,745	0,078
3σ statistical		0,008	0,020	0,038	0,048

TABLE 4. Determining the Parameters* of HgBr_2 with L = 660 mm

Expt. No.	R, %	$r_a(\text{Hg—Br}), \text{Å}$	$r_a(\text{Br—Br}), \text{Å}$	$l_m(\text{Br—Br}), \text{Å}$
1	6,65	2,380(4)	4,718(27)	0,089(36)
2	9,46	2,379(6)	4,727(33)	0,047(78)
3	7,29	2,379(4)	4,737(24)	0,051(54)
4	6,86	2,384(4)	4,744(24)	0,045(27)
5	7,34	2,375(4)	4,747(24)	0,077(42)
6	8,40	2,378(5)	4,762(33)	0,087(48)
7	7,54	2,383(4)	4,758(27)	0,063(48)
8	7,36	2,381(4)	4,746(30)	0,052(54)
9	8,06	2,383(5)	4,751(30)	0,068(51)
10	9,32	2,378(5)	4,722(45)	0,107(51)
11	8,54	2,382(5)	4,724(33)	0,077(51)
12	8,62	2,382(5)	4,768(33)	0,068(54)
13	9,50	2,382(5)	4,752(33)	0,063(63)
14	9,31	2,379(5)	4,758(36)	0,071(54)
15	10,41	2,376(6)	4,751(45)	0,092(54)
16	7,36	2,381(4)	4,749(30)	0,086(42)
17	8,27	2,377(5)	4,750(30)	0,065(54)
Mean		2,380	4,745	0,071
3σ statistical		0,007	0,043	0,052

*The parameter $l_m(\text{Hg—Br}) = 0.037$ was not varied because of the strong correlation with the other parameters.

TABLE 5. Weighting-Matrix Determination: W_1) Unit Matrix, W_2) Diagonal Matrix (element i inversely proportional to the measurement variance $sM(s)$ at point i), W) Complete Weighting Matrix

parameter	L = 420 mm; number of experiments 18			L = 660 mm; number of experiments 18			
	statistical mean	$sM(s)$ exp mean		statistical mean	$sM(s)$ exp mean		
		W_1	W_2		W_1	W_2	W
$R, \%$		7,80	10,02		5,64	6,37	5,68
scale		0,99	0,99		1,00	0,98	1,00
$r_a(\text{Hg}-\text{Br})$	2,383(8)	2,383(3)	2,378(7)	2,380(7)	2,380(3)	2,378(5)	2,378(5)
$l_m(\text{Hg}-\text{Br})$	0,037(20)	0,038(9)	0,033(3)	0,037	0,037	0,037	0,037
$l_m(\text{Br}-\text{Br})$	4,745(38)	4,745(21)	4,709(54)	4,745(43)	4,745(21)	4,743(30)	4,741(22)
$l_m(\text{Br}-\text{Br})$	0,078(48)	0,081(24)	0,110(78)	0,071(52)	0,073(33)	0,076(54)	0,070(45)

experiments were discarded because they did not satisfy the $3\sigma_{\text{stat}}$ rule. The calculated covariance matrix C was used in determining the weighting matrix $W = C^{-1}$ for the LS procedure:

$$\min Q = \sum_{i=1}^N \sum_{j=1}^N \omega_{ij} (y_i - k \cdot s_i M(s_i)) (y_j - k \cdot s_j M(s_j)),$$

where $y(s)$ is $sM(s)$, the experimental mean over all experiments. Table 5 gives the results.

CONCLUSIONS

The present study is part of a large program being conducted at the All-Union Scientific-Research Center for Properties of Surfaces and Vacuum involving electron-diffraction studies on polyatomic inorganic molecules. The unique data on the structures of oxygen-acid salts and complex halides have been included in reference tables [9] and used in calculating thermodynamic functions [10]. The difficulties in obtaining electron-diffraction patterns for these compounds do not allow one to perform a complete statistical analysis in each case, so the results here are of interest not only in themselves but also as regards interpreting molecular constants previously measured.

It was possible to perform a complete statistical analysis for the molecular constants of HgBr_2 because of the software for continuous automatic structure-parameter definition. It would be completely unrealistic to process separately the data from the 40 experiments without it.

The main results are as follows.

1. An effective method has been tested for distinguishing the molecular component of the scattering intensity.
2. A unified software suite has been written for interpreting electron-diffraction patterns based on a 3CS microdensitometer and an HP 21MX minicomputer (Hewlett Packard).
3. Complete statistical analysis for the HgBr_2 molecule has shown that the methods used at the center for processing electron-diffraction patterns lead to undistorted values for the internuclear distances and mean-square vibration amplitudes, together with somewhat underestimates of the errors.

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MASS-SPECTROMETRIC STUDY OF ION CLUSTERING IN ALKALI-METAL
 HYDROXIDE VAPOR: CLUSTER-ION ENERGY AND STRUCTURAL
 CHARACTERISTICS

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Various positive and negative ions have been recorded in the equilibrium vapors from alkali-metal hydroxides: M^{\pm} , OH^{-} , O^{-} , MO^{-} , MOH^{-} , and $X^{\pm}(MOH)_n$, where $X = M^{\pm}$, OH^{-} , $n = 1-6$. The equilibrium constants have been measured for $X^{\pm}(MOH)_n = X^{\pm} + nMOH(k)$, $n = 1-3$, and the enthalpies of reaction have been determined, from which the enthalpies of formation and dissociation energies of $X^{\pm}(MOH)_n$ have been calculated. The relative stabilities of the ions in the series from Na to Cs are examined.

INTRODUCTION

Cluster ions are important in solution chemistry, in various processes occurring in weakly ionized gases, in solvation, heteronuclear condensation, gas-phase electrolysis, and so on, and during the past two decades they have become the object of extensive research. Usually, by cluster ion is meant a system consisting of a central ion (the cluster-forming one) and surrounding atoms and molecules, which are held by the ion in the main by its electrostatic field [1]. Cluster ions should be divided into two types (molecular and ionic) from the bond type. In a molecular cluster (weakly bonded cluster ion), the bond is provided mainly by the long-range polarization interaction between the ion and atoms or molecules (this usually applies to a system consisting of an ion and atoms or of an ion and weakly polar molecules). A feature of such clusters is that the interactions between the components are relatively weak, so the components retain their individuality. An ionic cluster (strongly bonded cluster) is formed from an ion and highly polar molecules. Such a cluster has chemical (ionic) bonds, and the marked differences between the components are eliminated, so it is difficult to distinguish the ion and the molecules in their initial isolated forms within the system.

One of the most effective methods of examining clustering and the properties of cluster ions is mass spectrometry; two forms of method are widely used at present. The first of these is the effusion form (or ion-molecule equilibrium method), which was first proposed by Chupka [2], and it is intended for ionic cluster. The cluster ions are formed in an equilibrium hot vapor by the clustering of molecules from the vapor around simple ions formed by thermal ionization of a compound within an effusion cell at a pressure <10 Pa. Kebarle et al. [3] developed another form of the method and used it to examine molecular cluster ions. These are formed in a reaction chamber by collisions at an elevated pressure (up to 10^4 Pa) and involve molecules of a solvating agent (usually low-polarity H_2O , NH_3 , SO_2 , etc.) on various ions.

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