The inversion of diatomic spectra to estimates of population parameters

M. G. Prisant and R. N. Zare

Articles you may be interested in

An inverse method for estimating the electromechanical parameters of moving-coil loudspeakers
J. Acoust. Soc. Am. **134**, 3594 (2013); 10.1121/1.4824158

Estimations of Rotational Relaxation Parameters in Diatomic Gases
AIP Conf. Proc. **1333**, 1257 (2011); 10.1063/1.3562816

Parameter Estimation in Population Balance Models
AIP Conf. Proc. **1281**, 1971 (2010); 10.1063/1.3498319

Estimating parameter uncertainties in matched field inversion by a neighborhood approximation algorithm
J. Acoust. Soc. Am. **121**, 833 (2007); 10.1121/1.2427125

System parameter estimation in tomographic inverse problems
AIP Conf. Proc. **568**, 181 (2001); 10.1063/1.1381883

The inversion of diatomic spectra to estimates of population parameters

M. G. Prisant[a] and R. N. Zare[b]

Department of Chemistry, Stanford University, Stanford, California 94305

A bivariate polynomial representation of rovibrational population distributions is developed. This representation permits direct reduction of diatomic fluorescence spectra from chemical dynamics experiments to estimates of rotational and vibrational parameters by means of a linear least squares procedure.

I. INTRODUCTION

In principle, the use of laser fluorescence excitation or chemiluminescence emission under single collision conditions allows determination of the product internal state distribution of chemical reactions. In practice, however, experiments often cannot resolve the spectral features that directly report individual product state populations.

In cases where individual rovibrational populations are not resolved, the traditional approach for inferring population information has been computer simulation of a spectrum.[1,2] The simulated and empirical spectra are then compared and the population distribution varied iteratively until a suitable fit of the experimental data is obtained. Historically this approach has been implemented in an *ad hoc* fashion. Different groups have written simulation codes tailored to the spectroscopic transitions studied in their own experiments. A variety of functional forms have been used to describe the rovibrational population distributions.

There are, however, inherent shortcomings of the simulation approach which go beyond the historical lack of standardization. Guessing an appropriate population distribution and iterating by trial and error to a best-fit involves much effort and uncertainty. Error bounds of estimated parameters and sensitivity of the fit to the variation of estimated parameters are not quantitatively defined. Perhaps most importantly, simulation provides no protocol for assessing the level of population information which may be realistically inferred from a given set of experimental data.

The use of regression techniques for the analysis of chemiluminescence spectra has already been introduced.[3–6] Johnson, Kvaran, and Simons[3] have considered bound–free emission. Wright and Leone[4] and Ishikawa and Parson[5] have treated bound–bound transitions. However, in none of these studies has provision been made for fitting the form of the rotational distribution. This omission can lead to misestimation of the population parameters when the form of the spectrum depends on the rotational distribution.[6]

The ambiguities of population information extracted using existing methods have discouraged rigorous dynamical interpretation of experiments which produce highly overlapped spectra. This is especially frustrating because many of the systems most amenable to study by optical techniques—such as those reactions which produce alkaline earth monohalide products—are often characterized by very narrow rotational line spacings and hence exhibit highly congested spectra.[7,8]

In this work, we develop a comprehensive approach for the characterization and extraction of population information from incompletely resolved laser fluorescence excitation or chemiluminescence spectra. Our treatment brings together the following elements: development of linear functional forms for representing rovibrational population distributions which are not specific to a particular product or reaction; application of linear regression techniques for estimation of population parameters; and reconstruction of rovibrational population distributions using the estimated parameters. The regression procedure remedies the deficiencies inherent in simulation: it automates the search for a best-fit parameter set, gives confidence limits on estimated parameters, and defines the level of population information which may be extracted from a particular spectrum. A linear parametrization of the population distribution considerably reduces the computational cost of the regression procedure: only a single calculation of the spectrum is required for extraction of a best-fit parameter set.

We have written a general computer program which incorporates these features. Required as input are the molecular constants and vibrational band strengths for the transitions to be studied. In the simulation mode the program allows descriptions of the population distribution according to a number of functional forms; the inversion mode provides for direct reduction of digitized experimental spectra.

The use of the inversion procedure is illustrated with synthetic spectra typical of chemiluminescence emission from the reaction $Ca + F_2 \rightarrow CaF(B) + F$. This reaction has been studied in our own laboratory[9,10] as well as elsewhere.[11,12] It is an appropriate candidate for an inversion approach because the sheer number of states populated in $CaF(B)$—at least 30 vibrational levels and up to 200 rotational states in each of these vibrational levels—makes guessing a distribution particularly problematic. The behavior of the inversion procedure is investigated for variation of spectral resolution, signal to noise ratio, and sensitivity to the accuracy of molecular constants.

II. THEORY

A. Intensity as a function of wavelength

It may be shown that in the absence of saturation effects that intensity as a function of wavelength in both chemilu-

---

[a] Present address: Department of Chemistry, University of Toronto, Toronto, M5S 1A1, Canada.
[b] Holder of a Shell Distinguished Chair.

minescence and laser fluorescence excitation spectra is given by[7,11,13]

$$I(\lambda) = \sum_p NP(p)\sum_t S(p,t)R\,[\lambda - \lambda\,(p,t)], \qquad (1)$$

where p labels the states populated by the reaction, t the states optically coupled to the populated states, $I(\lambda)$ is the intensity of light measured at wavelength λ in units of photons/s, $P(p)$ is the relative population in state p, N is a normalization factor which scales the relative population to an absolute number of molecules, $\lambda\,(p,t)$ is the wavelength of the $p \rightarrow t$ transition, $S(p,t)$ is the strength of the transition in photons/s per molecule, and $R\,[\lambda - \lambda\,(p,t)]$ is the instrumental response function.

In the case of chemiluminescence, p labels the upper states and t labels the lower states which are optically coupled to p. The instrumental response is given by a monochromator slit function—we represent this as a triangle function[14]:

$$R\,[\lambda - \lambda\,(p,t)] = 1 - |[\lambda - \lambda\,(p,t)]/\Delta| \qquad (2a)$$

for $|[\lambda - \lambda\,(p,t)]| < \Delta$ and

$$R\,[\lambda - \lambda\,(p,t)] = 0 \qquad (2b)$$

for $|[\lambda - \lambda\,(p,t)]| \geqslant \Delta$, where Δ is the monochromator resolution.

In the case of laser fluorescence excitation, p labels the lower states and t the states optically coupled to p by the laser radiation field. The measured intensity must be integrated over observation direction and laser polarization and corrected for laser power and photomultiplier response.[15] Here, we represent the instrumental response function by a Gaussian:

$$R\,[\lambda - \lambda\,(p,t)] = \exp\{-[\lambda - \lambda\,(p,t)]^2/\Delta\}, \qquad (3)$$

where Δ is the laser bandwidth.[14] We note that in laser fluorescence excitation the validity of Eq. (1) depends on the uniformity of detector response for all states t at a given pump wavelength.

All further analysis derives from application of Eq. (1). Description of the generalized calculation of line positions and strengths in diatomic spectra has been given elsewhere.[16,17] In what follows, we develop a linear representation of the rovibrational population distribution, apply linear regression to estimate the population parameters, and use the estimated population parameters to reconstruct the rovibrational distributions.

B. The bivariate polynomial representation

A rovibrational distribution will in general depend on the vibrational quantum number v and the rotational quantum number J. Representing the distribution in terms of these independent variables is, however, inconvenient because the maximum v and J will differ for each reaction. Moreover, we must specify the rotational distribution for each vibrational state. Zamir, Levine, and Bernstein[13] introduce the following reduced forms for the independent variables of vibration and rotation:

$$f = E_{\text{vib}}/(E - E_{\text{el}}), \qquad (4)$$

$$g = E_{\text{rot}}/(E - E_{\text{el}} - E_{\text{vib}}), \qquad (5)$$

where E_{el} is the electronic energy, E_{vib} is the vibrational energy, and E_{rot} is the rotational energy of the molecule, all measured from the minimum of the ground state potential curve, and E is the reaction exoergicity. The f and g variables range between 0 and 1 and label states by the fraction of energy disposed into vibration or rotation. We note that the population in state v,J will be given by

$$P(v,J) = P(f,g)\mathscr{J}\,[(f,g)/(v,J)], \qquad (6)$$

where $P(f,g)$ is the probability of a given f and g and the second term is the Jacobian of f and g with respect to v and J. The f and g variables allow comparison between the population distributions of different reactions and provide a plausible means of globally describing the rovibrational distribution.

A bivariate polynomial in the reduced variables f and g yields a linear parametrization of the population distribution. Such a representation has the following form:

$$P(f,g) = \sum_{i,j} a_{ij} f^i g^j. \qquad (7)$$

The coefficients a_{ij} are the linear parameters of the fit. We note that the value of a_{00} affects only the normalization and may be set to a constant. The relative populations are a linear transformation of the coefficients; hence p populations determine $p - 1$ coefficients and a normalization factor. For the systems we have considered p is a very large number. In practice, the sum over i and j is terminated at a finite value.

In order to intuitively understand the meaning of the bivariate functional form we consider the case in which $P(f,g) = P(f)\cdot P(g)$, i.e., $P(f,g)$ is the product of two univariate distributions, $P(f)$ and $P(g)$. Let the univariate distributions be given by the quadratic forms:

$$P(f) = c_0 + c_1 f + c_2 f^2, \qquad (8)$$

$$P(g) = d_0 + d_1 g + d_2 g^2. \qquad (9)$$

The bivariate polynomial formed as the product is

$$P(f,g) = \sum_{i,j} c_i d_j f^i g^j. \qquad (10)$$

The interpretation of the bivariate coefficients involving separable and finite series univariate distributions is transparent and provides a rough guide to the meaning of the coefficients.

In the general case univariate distributions are determined by sums over the bivariate distribution:

$$P(f) = \sum_g P(f,g), \qquad (11)$$

$$P(g) = \sum_f P(f,g). \qquad (12)$$

It will prove convenient to introduce the variables $F_i = \sum_f f^i$ and $G_j = \sum_g g^j$. Then the univariate distributions in f and g may be written as

$$P(f) = \sum_i f^i \sum_j a_{ij} G_j \qquad (13)$$

and

$$P(g) = \sum_j g^j \sum_i a_{ij} F_i. \tag{14}$$

In the case where all coefficients of the bivariate distribution are determined Eqs. (13) and (14) may be used to exactly define the univariate distributions. When fitting the population parameters, we do not expect full determination of the bivariate distribution—therefore the form of the univariate distribution will have to be inferred from partial knowledge of the bivariate distribution.

C. Inversion of population distributions

For a detailed discussion of the formalism and assumptions of linear least-squares parameter estimation, the reader is referred to a number of standard texts.[18–20] Our concern here is to show the application of this formalism to the estimation of population parameters from fluorescence spectra.

1. Spectral intensity: A linear transformation of population parameters

We begin by recasting the expression for intensity as a function of wavelength into an appropriate form for linear regression. Substituting the bivariate functional form into Eq. (1) we find

$$I(\lambda) = \sum_{i,j} a_{ij} \sum_{p,t} N f^i g^j S(p,t) R[\lambda - \lambda(p,t)] \mathscr{S}[(f,g)/(v,J)], \tag{15}$$

where a_{ij} are the unknown bivariate polynomial coefficients and the interior sum over p,t may be calculated from molecular constants and instrumental parameters.

Define the vector I to be the set of n calculated intensities such that:

$$I = [I(\lambda_1), I(\lambda_2), ..., I(\lambda_n)] \tag{16}$$

and the vector b to be the set of k bivariate polynomial coefficients such that

$$b = [b_1, b_2, ..., b_k]. \tag{17}$$

A common error in the formulation of inversion problems is the attempt to fit too many model parameters. For the fitting procedure to be meaningful, the number of observations n should be much larger than the number of parameters k to be optimized. Though this condition is usually easily fulfilled in fluorescence spectra—there are generally hundreds of measured intensities—we point out that it is best to construct a model which carefully chooses the parameters to be optimized.

The calculated spectrum may now be represented in matrix notation by

$$I = Mb, \tag{18}$$

where M is the model matrix of dimension n by k. This matrix is called the model matrix because it contains our explanation for the observables. The elements of M are given by

$$M_{rs} = N \sum_{p,t} f^{i(s)} g^{j(s)} \mathscr{S}\{(f,g)/[v(p),J(p)]\}$$

$$\times S(p,t) R[\lambda - \lambda(p,t)], \tag{19}$$

where index r refers to the wavelength position and index s determines the particular combination of i and j chosen.

2. Population parameters through linear regression

Call the vector of intensities measured in the experiment Y. Because of measurement uncertainties and imperfections in the model, we expect that the measured spectrum will differ from the calculated spectrum. The true variance of the measurement errors will in general be unknown at the outset and must be estimated as part of the regression procedure.

We write

$$Y = Mb + \epsilon, \tag{20}$$

where ϵ is the vector representing the difference between the measured and calculated intensities. We wish to find the set of parameters b which minimizes the square of the difference between measured and calculated intensities. This may be shown to be given by[20]

$$\hat{b} = (M^T M)^{-1} M^T Y, \tag{21}$$

where superscript T indicates the transpose of the matrix, superscript -1 indicates the inverse of the matrix, and superscript circumflex is the standard statistical notation for the estimated value. In linear regression, the best-fit parameter set is uniquely determined.

The best-fit parameter set $\hat{b}$ fixes the minimum root-mean-square of the residuals. This is given by $(n^{-1} \hat{\epsilon}^T \hat{\epsilon})^{1/2}$ so that

$$\hat{\epsilon} = Y - M\hat{b}. \tag{22}$$

An unbiased estimate may now be derived for the unknown variance of the measured observables such that

$$\hat{\sigma}^2 = (n - k)^{-1}(\hat{\epsilon}^T \hat{\epsilon}). \tag{23}$$

The associated estimate of the standard deviation of the measurement error is simply the square root of the variance. The quantity $(n - k)$ determines the number of degrees of freedom in the least squares fit.

We now describe the errors in the best-fit parameters. Let us define the variance–covariance matrix $\hat{\theta}$ by

$$\hat{\Theta} = \hat{\sigma}^2 (M^T M)^{-1}. \tag{24}$$

The diagonal elements $\hat{\theta}_{ss}$ define the estimated variances in the best-fit parameters. The standard error in estimated parameter s is given by $\hat{\theta}_{ss}^{1/2}$. The 95% confidence limits for the true value of the estimated parameter, assuming errors are normally distributed about the mean value, are given by

$$\hat{b}_s \pm 2\hat{\theta}_{ss}^{1/2}. \tag{25}$$

In general, if the confidence limits for an estimated parameter include zero, then this parameter cannot be significantly fitted. The parameter in question should be set to zero and the linear regression redone. This protocol defines, in a practical sense, the maximum extent of information with statistical significance that one may extract from an overlapped spectrum.

The off-diagonal elements of the variance–covariance matrix $\hat{\theta}_{sw}$ determine the estimated covariances. These are often normalized and reported as

$$\hat{C}_{sw} = \hat{\theta}_{sw}/(\hat{\theta}_{ss}\hat{\theta}_{ww})^{1/2}, \tag{26}$$

where $\hat{C}_{sw}$ is the correlation between the estimate of parameter s and parameter w. The correlation coefficient ranges between -1 and $+1$. If the estimates of the two parameters

are closely correlated then $|\hat{C}_{sw}|$ approaches 1; if uncorrelated it approaches 0. The values of the correlation coefficients are a function of the model structure rather than measurement precision. If two parameters are closely correlated, then they cannot be independently determined. An example of this would occur in the case of a bivariate distribution formed by two independent univariate distributions: we would expect the cross terms to be highly correlated with the terms of single variables.

Linear least squares formally assumes that the model perfectly describes the physical situation and that differences between model predictions and experimentally measured intensities are due to random (i.e., noise distributed according to a Gaussian distribution) errors. Systematic errors may be introduced from two sources: inability of the bivariate polynomial to exactly reproduce the functional form of the actual distribution and inaccuracies in the calculated line positions and strengths. In practice, we find the later cause to be the major source of systematic error as will be illustrated in the examples. Inaccuracies in the calculated line positions and strengths may come from insufficient precision in the molecular constants, errors in the rotational line strengths and positions due to perturbations, and inaccuracies in the vibrational band strengths due to rotational dependence of Franck–Condon factors and variation of the transition dipole moment with internuclear distance. While the inversion method developed here does not provide for optimization of molecular constants and Franck–Condon factors, the method may be used to distinguish the relative quality of different input data sets. The strength of the calculated model and the relative quality of the input data may be evaluated by consideration of the RMS deviation between model and data.

3. Estimation of univariate populations

The linear regression analysis will, in general, yield a partial set of significantly fitted coefficients. For a given functional form, this partial set is uniquely determined, i.e., changing the value of any of the fitted coefficients will cause the root-mean-square of the residuals to increase. Though the regression procedure properly estimates population parameters rather than distributions, we would like to reconstruct the distributions from the estimated parameters.

Two seeming ambiguities, however, now arise. First, significant parameter values may be estimated for a number of different functional forms, i.e., those involving different powers in f and g. Second, neither the bivariate population distribution nor the univariate distributions will be uniquely determined by a given partial minimum variance set of coefficients.

A full treatment of these questions is outside the scope of this paper and will be developed in a companion article.[21] For the spectra which we have considered, the choice of bivariate polynomial terms is largely determined by the parameters which can be significantly fitted: generally this involves terms at most third order in f, first order in g, and cross terms linear in g. In practice, we find that one very quickly develops an intuition for which terms can be significantly fit.

The partial set of fitted coefficients incompletely determines both the bivariate and univariate distributions. Any method for reconstruction of the actual distributions will rely on extrapolation of this partial information. The simplest extrapolation is to take the truncated bivariate functional form determined by the significantly fitted parameters to represent the actual distribution. The univariate distributions are determined by truncating the sums given in Eqs. (13) and (14) to only include significantly fitted terms. The standard errors in the propagated estimates of the univariate are given by

$$E(f) = \sum_i f^i \sum_j e_{ij} G_j, \qquad (27)$$

$$E(g) = \sum_j g^j \sum_i e_{ij} F_i, \qquad (28)$$

where $e_{ij} = \hat{\theta}_{ss}^{1/2}$, the standard error in the estimated value of a_{ij} or parameter s.

III. RESULTS AND DISCUSSION

In this section, we illustrate the sensitivity of emission spectra to the form of the population distribution, demonstrate the practicability of the inversion technique, and consider the sensitivity of the recovered population distributions to parameter choice, resolution, noise, and the accuracy of molecular constants. We use synthetic spectra representative of the chemiluminescence emission from the reaction of $Ca + F_2 \rightarrow CaF(B) + F$[9,22] to characterize the inversion technique and to understand the sensitivity of population information to experimental conditions. The population analysis of empirical spectra using the inversion technique
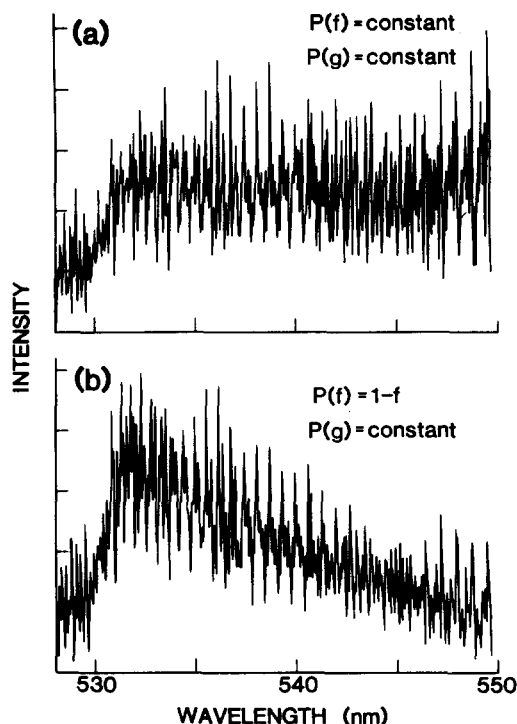

FIG. 1. Sensitivity of the simulated CaF B–X $\Delta v = 0$ chemiluminescence spectrum to the form of the vibrational distribution: (a) $P(f)$ = constant; and (b) $P(f) = 1 - f$. In these cases $P(g)$ is constant. The intensity is in arbitrary units.

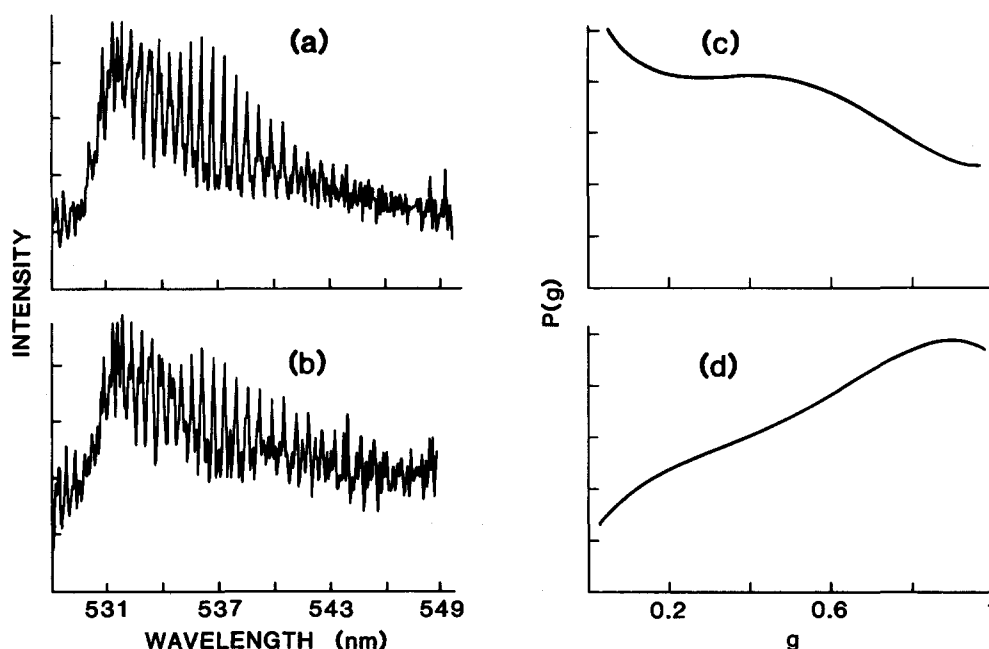FIG. 2. Sensitivity of simulated CaF B–X $\Delta v = 0$ chemiluminescence spectrum to the form of the rotational distribution. The rotational distribution for (a) and (b) differ and are presented in (c) and (d), while the vibration distributions are the same and given by $P(f) = 1 - 2.32f + 4.52f^2 + 6.17f^3 + 3.04f^4$.

and the details of using the inversion program which we have written are described elsewhere.[9]

All CaF $B\,^2\Sigma$–$X\,^2\Sigma$ spectra presented share the following characteristics: only the $\Delta v = 0$ sequence is considered, spectral resolution is set at 0.05 nm unless otherwise stated, molecular constants for the synthesis of the spectrum are taken from Bernath, Dulick, and Field,[23] Franck–Condon factors are obtained from the work of Menzinger,[11] the exoergicity of the reaction is set to 35 000 cm^{-1}, the maximum v level to 35, and the maximum J level to 250.

A. Sensitivity of spectra to the form of the population distribution

The sensitivity of the emission spectrum to the form of the vibrational distribution is shown in Fig. 1. In both spectra, the rotational distribution in g is set such that $P(g) = $ constant. In Fig. 1(a), note the vibrational distribution is also constant, while in Fig. 1(b), the vibrational distribution is set to a straight line of the form $P(f) = 1 - f$. As expected, the spectrum shows strong dependence on the form of the vibrational distribution: attenuation of high-lying vibrational levels is mirrored in attenuation of the emission spectrum to the red.

The sensitivity of the emission spectrum to the form of the rotational distribution is shown in Fig. 2. We note that, in general, the shape of the spectrum is less sensitive to the form of the rotational distribution than it is to that of the vibrational distribution. The example shown here, however, demonstrates that changes in the form of the rotational distribution can visibly alter the shape of the overall emission spectrum.

The above examples demonstrate that certain traditional assumptions concerning emission spectra are not sufficient for quantitative characterization of population information. First, even in the case where the form of the rotation distribution is held constant, it is difficult to characterize the form of the vibrational population distribution by the rela-

tive peak-to-valley height of the vibrational bandheads. Specifically in Fig. 1(a), the peak-to-valley height is not given by the product of the Franck–Condon factor times the vibrational population. Second, the overall shape of the spectrum reflects the rotational distribution. The broad form—as opposed to the individual sharp features—appears to carry much of the population information.

B. Inversion of test spectra

We demonstrate the inversion technique by using the linear regression procedure to recover population information from CaF B–X synthetic emission spectra. A noise level corresponding to 1% of the maximum peak height is added to the spectra. These spectra are inverted to estimates of population parameters. The univariate distributions are
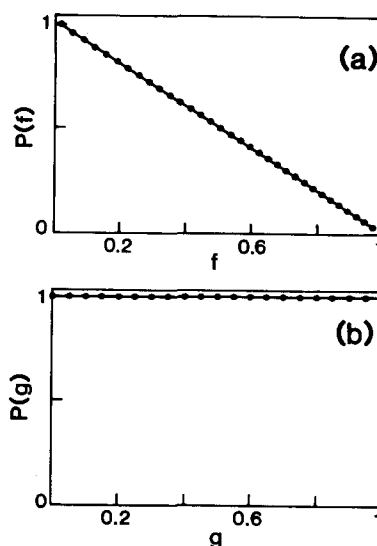

FIG. 3. Inversion of CaF chemiluminescence spectrum: (a) vibrational distribution and (b) rotational distribution. The solid circles are the input populations; the solid lines are the recovered distributions.
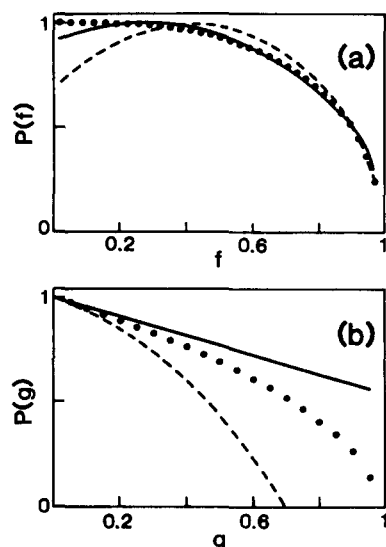
FIG. 4. Inversion of simulated CaF $B-X$ spectrum using different population parameter sets: (a) vibrational distribution; and (b) rotational distribution. The solid circles are the input populations; the dashed lines represent the recovered populations when all parameters of a quadratic polynomial in f and g are allowed to vary; and the solid lines represent the recovered populations when the statistically insignificant g^2 parameter is removed.

then reconstructed from a truncated bivariate polynomial using the estimated parameters.

We begin by considering examples in which all parameters of a quadratic bivariate distribution are fitted. Figure 3 shows the ability of the program to recover information in the undemanding cases where the rotational distribution is held constant and the vibrational distribution is set to $P(f) = 1 - f$. The population distributions in this instance

are recovered almost exactly.

Not all distributions allow significant determination of every parameter of a quadratic bivariate polynomial. In such cases, we eliminate the parameters whose confidence limits include zero and allow the remaining parameters to vary. This situation is illustrated in Fig. 4. The spectra are synthesized such that $P(f) = (1 - f^3)^{1/2}$ and $P(g) = (1 - g)^{1/2}$. The dashed lines represent the recovered population distributions when the parameters of the bivariate distribution are allowed to vary. Inspection of the variance–covariance matrix reveals that terms involving g^2 are not significantly fitted. When these terms are omitted, and other terms allowed to vary, the solid line is obtained.

The omission of the insignificant terms results in a better fit to the vibrational distribution and a nominally better fit to the rotational distribution. Note again that the form of the rotational distribution can influence the accuracy with which the vibrational populations are determined.

The form of the presumed population distribution can influence the choice of parameter terms for fitting. This can be seen by considering the inversion of a synthetic spectrum constructed from a bimodal distribution in vibration, as illustrated in Fig. 5. Recovery of a bimodal distribution requires a function form in f which allows for two extrema, i.e., is at least of cubic order. A first attempt to invert the spectrum using terms only up to quadratic order in f yields a RMS fit of 17.2 in arbitrary units. The recovered distribution indicates bimodality but does not reproduce the form of the initial distribution. A second attempt incorporating terms up to cubic order reduces the RMS variance to 3.3 and substantially recovers both the original vibrational and rotational distributions. The dramatic reduction in the RMS is the signature of finding the best distribution.
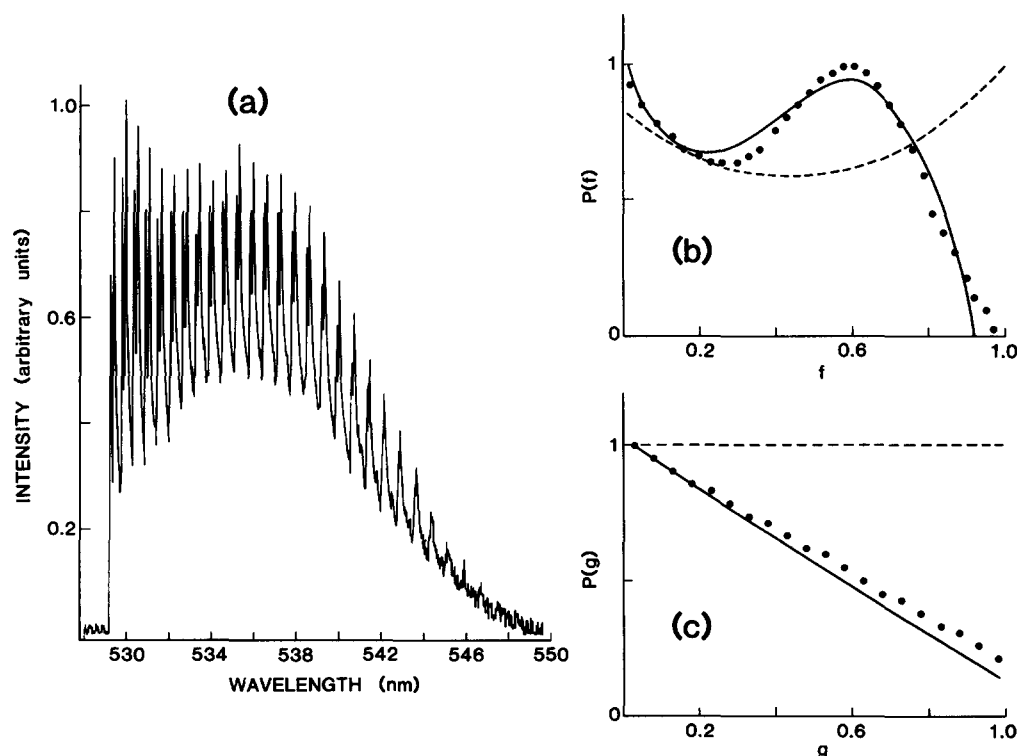

FIG. 5. Recovery of a bimodal distribution: (a) input CaF $B-X$ emission spectrum: resolution 0.05 nm. The spectrum has been synthesized according to the input distributions shown in panels (b) and (c) of this figure, normalized to a maximum peak height of 1.0, and been given a 1% noise level relative to the maximum peak height; and (b) vibrational distribution: input distribution is indicated by solid circles; recovered distribution when the linear and quadratic terms in f are fit is indicated by a dashed line, when the linear, quadratic, and cubic terms in f are fit is indicated by a solid line; and (c) rotational distribution: input distribution is indicated by solid circles; recovered distribution by a dashed line or a solid line, the same as in (b).
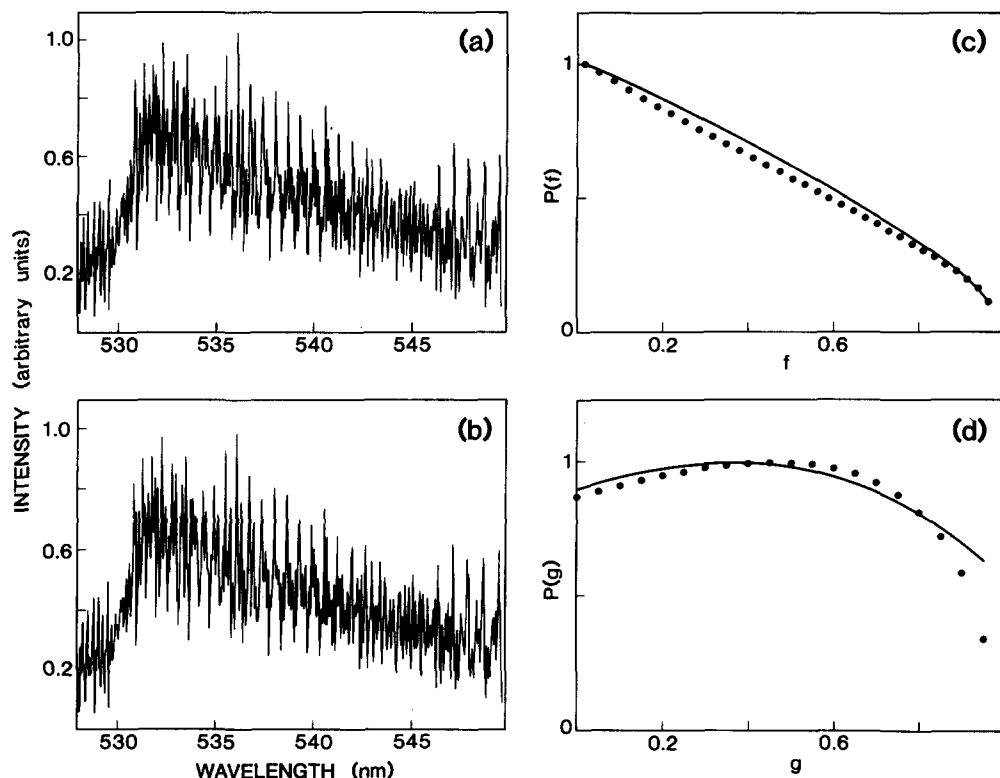
FIG. 6. (a)Input CaF $B-X$ emission spectrum: resolution 0.05 nm. The spectrum has been synthesized according to the input distributions shown in panels (c) and (d) of this figure, normalized to a maximum peak height of 1.0 and been given a 1% noise level relative to the maximum peak height. (b) Recovered CaF $B-X$ emission spectrum: resolution 0.05 nm. This spectrum has been synthesized according to the recovered rovibrational distributions shown in panels (c) and (d) of this figure. Input and recovered spectra are distinguished only by subtle fluctuations about the peak amplitudes.

C. Resolution, noise, and molecular constants

We now consider the sensitivity of the inversion method to the resolution, signal-to-noise ratio, and accuracy of the molecular constants. Our point of comparison is a synthetic chemiluminescence spectrum of the CaF $B\,^2\Sigma - X\,^2\Sigma$ transition characterized by 0.05 nm resolution, 1% noise level relative to the maximum peak intensity, and a rovibrational population distribution given by

$$P(f)P(g) = (1 - f)^{1/2}\exp(-f)(1 - g)^{1/2}\exp(g). \qquad (29)$$

The characteristics of the reference spectrum strongly resemble those of the experimental spectrum.[9,10,22] The synthesized spectrum having the above characteristics is displayed in Fig. 6(a).

Figure 6(b) shows the spectrum synthesized according to the population distributions recovered from the inversion of the spectrum in Fig. 6(a); Figs. 6(c) and 6(d) show the synthesized and recovered vibrational and rotational distributions, respectively. The inversion procedure is used to determine all eight terms of quadratic bivariate polynomial in f and g: all recovered coefficients are significant to one standard error. The estimated variance is 2.4 in arbitrary units. The input spectrum and the spectrum synthesized according to the recovered distributions are essentially visually indistinguishable—the differences are manifest in subtle fluctuations about the intensity amplitudes.

The chosen reference spectrum allows significant determination of bivariate population parameters up to second order in both f and g. Basically this corresponds to determining the mean and width of both the vibrational and rotational distributions. The reconstruction of the univariate distributions will depend on the extent to which their forms can be determined by these moments.

Figures 7 and 8 show the eight-parameter recovered dis-

tributions for resolutions of 0.1 and 0.2 nm, respectively. The estimated variance of the spectrum does not change appreciably with the change in resolution. However, the recovered distributions show a trend toward erosion of the quadratic component precision in the rotational distribution and to a lesser extent in the vibrational distribution.
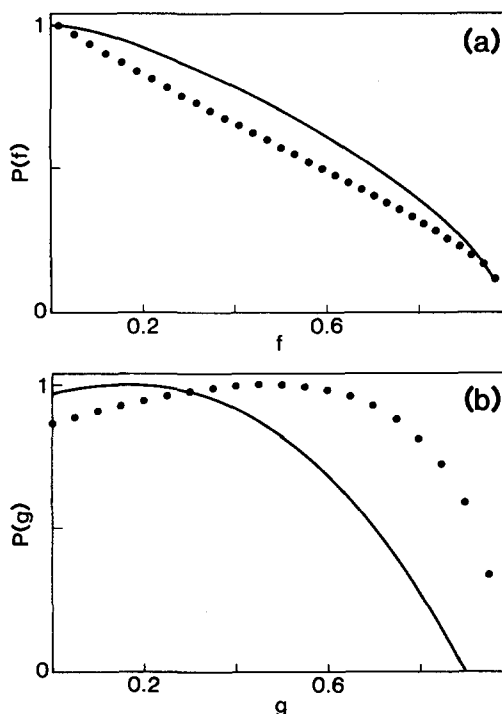

FIG. 7. Recovered eight-parameter rovibrational population distribution for 0.1 nm resolution, 1% noise level: (a) univariate distribution in vibration; and (b) univariate distribution in rotation.
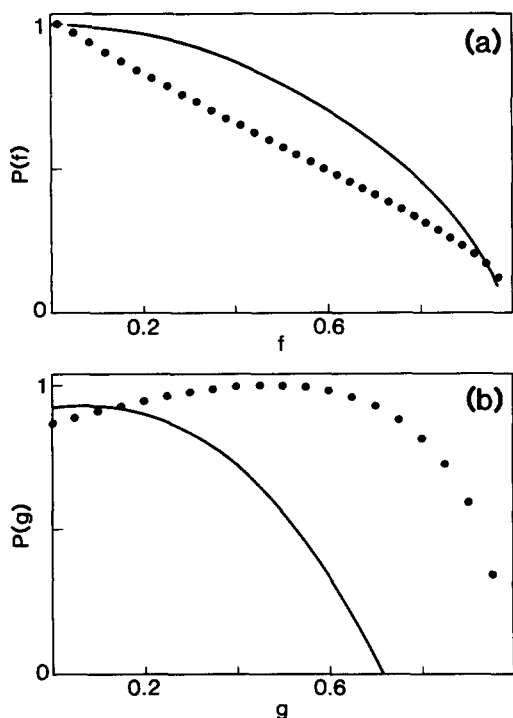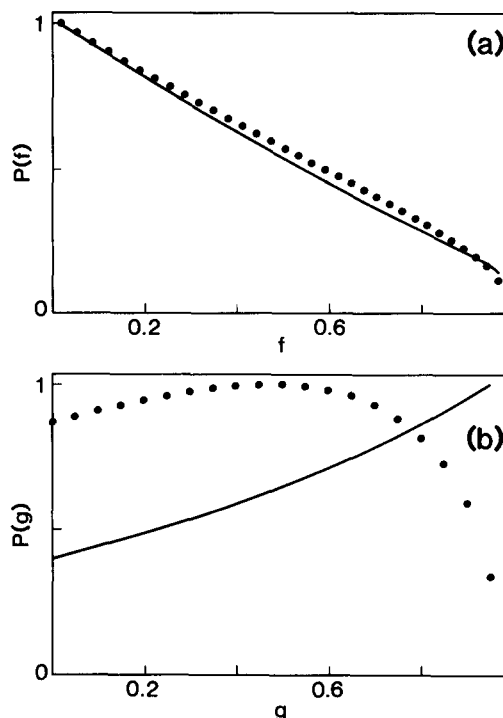
FIG. 8. Recovered eight-parameter rovibrational population distribution for 0.2 nm resolution, 1% noise level: (a) univariate distribution in vibration; and (b) univariate distribution in rotation.

FIG. 10. Recovered eight-parameter rovibrational population distribution for 0.05 nm resolution, 5% noise level: (a) univariate distribution in vibration; and (b) univariate distribution in rotation.

In the reference spectrum, the vibrational bandhead structure with peaks separated by approximately 0.5 nm is well resolved. The rotational contour of each bandhead feature of approximate width 0.1–0.2 nm is only partially resolved. Simple calculations show that approximately up to
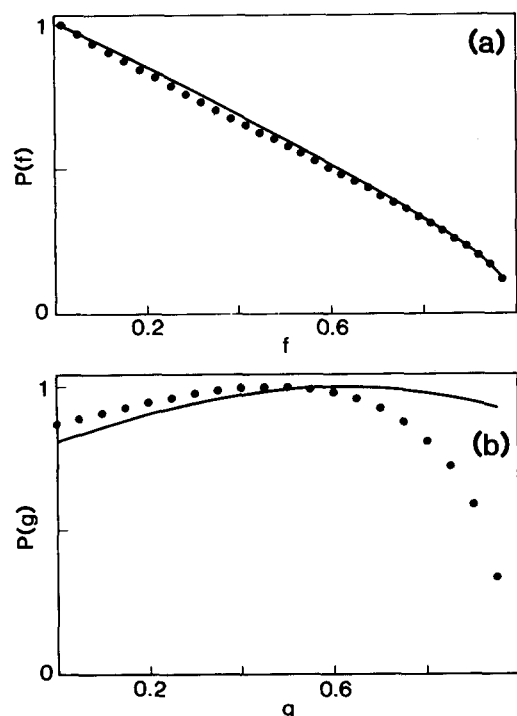

FIG. 9. Recovered eight-parameter rovibrational population distribution for 0.05 nm resolution, 2% noise level: (a) univariate distribution in vibration; and (b) univariate distribution in rotation.

ten vibrational transitions and 100–1000 rotational lines from each vibrational transition will contribute to the intensity at any given wavelength. Our resolution studies suggest that all the vibrational population information resides in the overall contour of the spectrum and is not terribly sensitive to variation of resolution. On the other hand, some of the rotational population information appears to reside in partial resolution of the band contours: the reconstructed rotational distribution is degraded with respect to the original as the resolution is varied between 0.05 and 0.2 nm.

Figures 9 and 10 show the recovered eight-parameter distributions for a noise level of 2% and 5%, respectively. At 2% noise level the estimated variance between synthesized and reconstructed spectrum is not appreciably different than that of the reference spectrum; at 5% noise level the variance approximately doubles. The recovery of the vibrational distribution appears unaffected by the change in noise level. The recovery of the rotational distribution is strongly eroded as the noise level increases to 5% of the maximum peak height.

Recovery of population distributions is not seriously degraded by noise levels less than 2% of the maximum peak height. Most of the variance in the recovered spectrum for low noise levels appears to originate in the inability of a quadratic bivariate polynomial to precisely reproduce the population distributions used to synthesize the spectrum. Above 2%, the noise in the spectrum begins to dominate the variance in the reconstructed spectrum. Recovery of the vibrational distribution seems highly insensitive to variation of noise level in the synthetic spectrum. The recovery of the rotational distribution is, however, degraded by high noise levels.
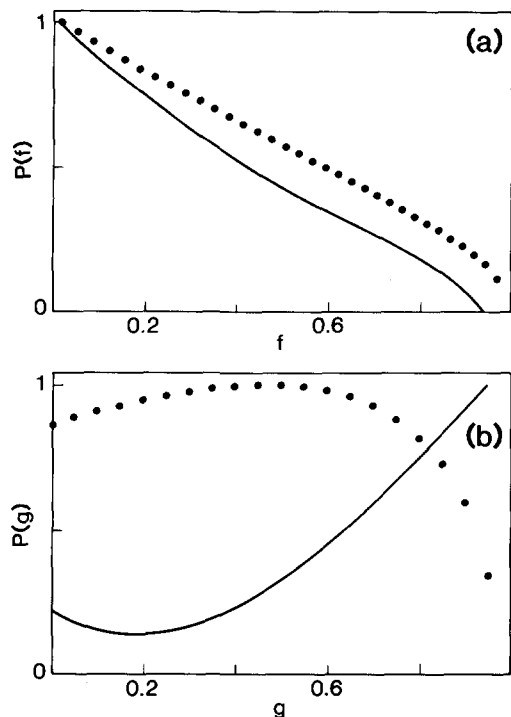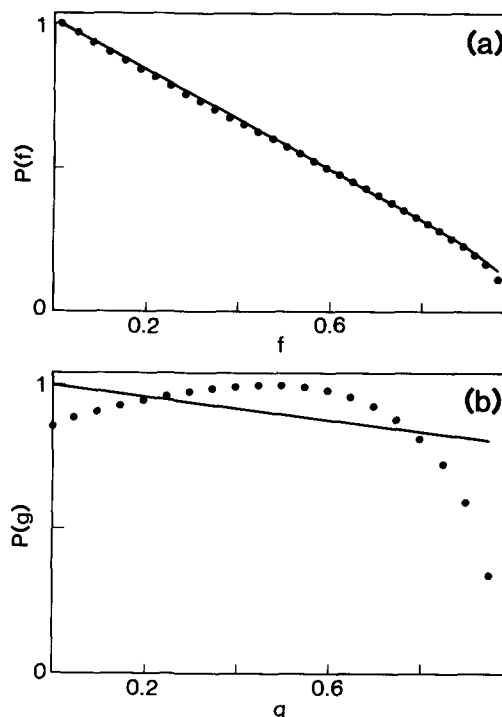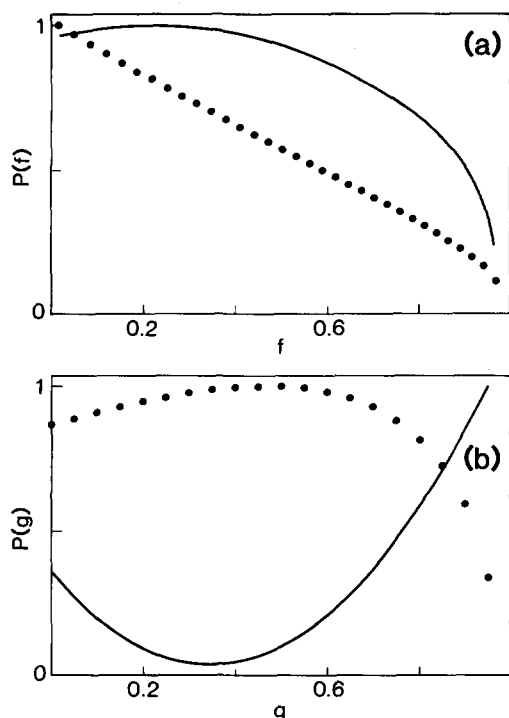
FIG. 11. Recovered six-parameter rovibrational population distribution for 0.05 nm resolution, 1% noise level: (a) univariate distribution in vibration; and (b) univariate distribution in rotation. The synthesized spectrum uses upper state B_v values determined by α_e equal to 0.0026; the inversion uses $\alpha_e = 0.0025$.

FIG. 13. Recovered three-parameter rovibrational population distribution for 0.05 nm resolution, 1% noise level: (a) univariate distribution in vibration; and (b) univariate distribution in rotation. The synthesized spectrum uses upper state B_v values determined by α_e equal to 0.0026; the inversion uses $\alpha_e = 0.0000$.

Figures 11 and 12 show the recovery of population information when inaccurate rotational constants are used to invert the synthetic spectrum. The spectra are synthesized using upper state B_v values given by $B_v = 0.342 - 0.0026(v + \frac{1}{2})$: Fig. 11 shows the six-parameter population distributions recovered using $B_v = 0.342 - 0.0025(v + \frac{1}{2})$, and Fig. 12 shows those recovered using $B_v = 0.342 + 0.000(v + \frac{1}{2})$. Corruption of the B_v values causes a marked increase in the estimated variance of the reconstructed spectrum: for $\alpha_e = 0.0025$ the variance is 140, and for $\alpha_e = 0.000$ it is 230. This increase in variance is caused by the misalignment of the bandheads in the reconstructed spectrum with respect to those of the synthesized spectrum. The rotational distribution is very poorly recovered in both cases. The recovery of the vibrational distribution is eroded with increasing error in the B_v value. A better fit to the vibrational distribution can be achieved by setting the poorly fitted g and cross-term parameters to 0; the recovered three-parameter distribution for $\alpha_e = 0.0$ is shown in Fig. 13. Figure 14 shows the comparison between input and recovered spectrum in the case of bad molecular constants. There are substantial differences in both peak positions and intensity amplitudes.

A marked increase in the variance of the reconstructed spectrum characterizes the loss of accuracy in the molecular constants used to invert the spectrum. In practice the variance in reconstructed experimental spectra as opposed to synthetic spectra should provide a sensitive measure of the accuracy of the molecular constants used. Recovery of rotational population information is severely degraded by inaccurate rotational constants. Remarkably, however, even in

FIG. 12. Recovered six-parameter rovibrational population distribution for 0.05 nm resolution, 1% noise level: (a) univariate distribution in vibration; and (b) univariate distribution in rotation. The synthesized spectrum uses upper state B_v values determined by α_e equal to 0.0026; the inversion uses $\alpha_e = 0.0000$.
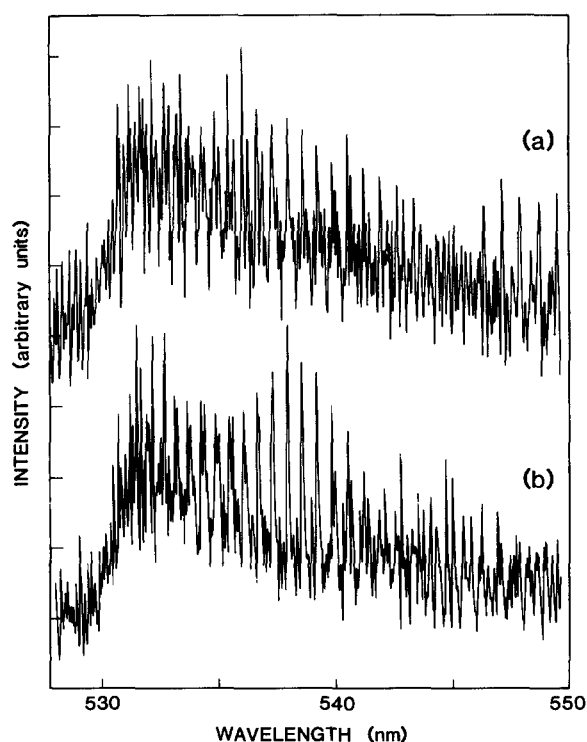
FIG. 14. Comparisons between (a) input spectrum shown in Fig. 6(a) and (b) recovered spectrum synthesized according to the rovibrational distributions and "bad" B_v values described in Fig. 12. The spectra are clearly distinguishable in both their peak heights and positions.

the case of highly corrupted constants it was still possible to recover the essential features of the vibrational distribution.

IV. SUMMARY

A linear regression procedure permits direct inversion of diatomic spectra to estimates of population parameters. The recovery of population distributions from congested spectra demands treatment of the following problems: calculation of line positions and strengths, development of a linear parametrization of internal state population, use of linear regression to extract the population parameters, and reconstruction of the population distributions using the estimated parameters.

In this work, these general problems have been treated with the specific objective of inverting the spectra of highly excited alkaline earth monohalide molecules. Our primary concern has been the recovery of rovibrational distributions in which there are a large number of vibrational as well as rotational levels. To this end we have not treated branching into fine structure components, Λ doublet components, or rovibrational distributions which populate few vibrational levels and many rotational levels. These problems will require further development of the population distribution representation. We have also been concerned with systems in which the molecular constants are fairly well characterized: the assumptions of the fitting procedure break down if the line positions cannot be calculated to reasonable accuracy.

We stress that, properly, the regression procedure determines parameters of a distribution rather than the form of the distribution itself. The questions of interpretation of fitted parameters and the reconstruction of distributions will be considered more fully in another article.[21]

We have studied a number of practical difficulties likely to be encountered by the experimentalist: poor resolution, inadequate molecular constants, and poor signal-to-noise. The results presented for the recovery of population distributions from synthetic spectra show that the inversion procedure is highly robust and forgiving. We are therefore encouraged that the inversion technique will provide molecular dynamicists with a quantitative and standardized means of deriving population information from molecular spectra.

ACKNOWLEDGMENTS

[1] Ch. Ottinger and J. Simonis, Phys. Rev. Lett. 35, 925 (1975).
[2] D. M. Manos and J. M. Parson, J. Chem. Phys. 69, 231 (1978).
[3] K. Johnson, A. Kvaran, and J. P. Simons, Mol. Phys. 50, 981 (1983).
[4] C. A. Wight and S. R. Leone, J. Chem. Phys. 78, 4875 (1983).
[5] T. Ishikawa and J. M. Parson, J. Chem. Phys. 79, 4261 (1983).
[6] M. G. Prisant and R. N. Zare in Gas-Phase Chemiluminescence and Chemi-ionization, edited by A. Fontijn (North-Holland, Amsterdam, 1985), pp. 189–202.
[7] J. L. Kinsey, Annu. Rev. Phys. Chem. 28, 349 (1977).
[8] M. Menzinger, Adv. Chem. Phys. 42, 1 (1980).
[9] M. G. Prisant, C. T. Rettner, and R. N. Zare, Chem. Phys. Lett. 88, 271 (1982).
[10] M. R. Corbett, M. G. Prisant, and M. Menzinger (in preparation).
[11] M. Menzinger, Chem. Phys. 5, 350 (1974).
[12] F. Engelke, Chem. Phys. 5, 350 (1974).
[13] E. Zamir, R. D. Levine, and R. B. Bernstein, Chem. Phys. 55, 55 (1981).
[14] W. Demtröder, Laser Spectroscopy (Springer, New York, 1982).
[15] R. Altkorn and R. N. Zare, Annu. Rev. Phys. Chem. 35, 265 (1984).
[16] D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, Mol. Spectrosc. 46, 37 (1973).
[17] R. N. Zare in Molecular Spectroscopy: Modern Research, edited by K. N. Rao and C. W. Mathews (Academic, New York, 1972), pp. 207–221.
[18] N. R. Draper and H. Smith, Applied Regression Analysis (Wiley, New York, 1966).
[19] W. C. Hamilton, Statistics in the Physical Sciences (Ronald, New York, 1964).
[20] D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, in Molecular Spectroscopy: Modern Research, edited by K. N. Rao (Academic, New York, 1976), Vol. II, pp. 1–67.
[21] M. G. Prisant and R. D. Levine (in preparation).
[22] M. G. Prisant, C. T. Rettner, and R. N. Zare, J. Chem. Phys. 81, 2699 (1984).
[23] P. F. Bernath, M. Dulick, and R. W. Field, Can. J. Phys. 58, 703 (1980).