OURNAL OF MOLECULAR SPECTROSCOPY **156,** 1–7 (1992)

The Reduction of Vibration–Rotational Spectral Data of Diatomic Molecules; $^{27}Al^{19}F$ $X\,^1\Sigma^+$ as a Test Case

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We have determined the coefficients $c_j, j \leqslant 6$, defining the potential-energy function $V(z)$, the term coefficients Y_{kl}, and other spectral parameters of AlF in the electronic ground state $X\,^1\Sigma^+$ by a direct fit of the published frequencies and wavenumbers of pure rotational and vibration–rotational transitions. We compare the values of the derived coefficients Y_{kl} and their associated standard errors with those reported from a direct fit of the same spectral data, in relation to the significance of spectral parameters determined in the process of reduction of vibration–rotational spectra. The direct fit to the potential-energy coefficients is demonstrated to provide not only a more compact and more physically meaningful representation, but also to produce a (slightly) smaller standard deviation of the fit. The resulting potential-energy function is valid in the range of internuclear distance $1.48 \leqslant R/10^{-10}\ \mathrm{m} \leqslant 1.90$.

The combined use of digital computers and interferometers having high spectral resolving power that enable effectively the simultaneous measurement of thousands of vibration–rotational spectral lines due to a particular chemical species produces commonly large sets of data, such that printing tables of the frequencies of the lines became impracticable for journals. Under these conditions it is imperative to be able to reduce the spectra so that the frequencies (or equivalently wavenumbers) of the lines are reproduced accurately by means of relatively few parameters according to some systematic model or procedure. Dunham enabled such a systematic reduction when he introduced (*1*) the term coefficients Y_{kl} in a relation for the vibration–rotational terms

$$E_{vJ} = \sum_{k=0} \sum_{l=0} Y_{kl}(v + \tfrac{1}{2})^k [J(J+1)]^l, \tag{1}$$

which is formally applicable to molecules of a single isotopic specification and in an electronic state of type $^1\Sigma$. The practical advantage of this relation is that it is linear in the parameters Y_{kl} that can thus be determined directly according to a well defined statistical procedure, for instance (and most commonly), weighted linear regression; the subscripts k and l assume the values of sufficiently large integers that the measured frequencies are reproduced within the experimental error of the measurements. The disadvantages of this representation are that it is merely a fitting to a double power series, lacking any underlying physical model whatsoever (*2*), and that there may eventually arise problems of convergence of the truncated polynomials.

Dunham also provided a physical model for the molecule as a rotating vibrator (*1*); the vibrational motion is governed by a function for the internuclear potential energy that he expressed in the flexible form of a truncated polynomial

$$V(x) = a_0 x^2 (1 + \sum_{j=1} a_j x^j), \tag{2}$$

0022-2852/92 $5.00

in which the variable $x = (R - R_e)/R_e$ denotes reduced displacement of the internuclear distance R from the equilibrium distance R_e; sufficient terms containing the coefficients a_j are taken in the sum to represent the potential energy according to the extent of the vibrational states between which spectral transitions are assigned. Within the approximation that electronic and nuclear motions within a molecule are considered separable, the effective potential-energy function for the internuclear motion is a fundamental molecular property, characteristic of a specific electronic state and independent of, or insensitive to, the particular nuclear masses (isotopic substitution). Dunham related the term coefficients Y_{kl} to the coefficients a_j in the potential energy; the coefficients Y_{kl} are in general functions of not only the coefficients a_j, $j > 0$, but also the harmonic vibrational parameter ω_e and the equilibrium rotational parameter B_e, with $a_0 = \omega_e^2/(4B_e)$. Between the transition frequencies ν and the parameters a_j, ω_e, and B_e there exist highly nonlinear relationships (*1*); indirect, or iterative, methods of the fitting of these parameters become accordingly necessary. Moreover the relationships between the term coefficients Y_{kl} and the potential-energy coefficients a_j are internally consistent if only the potential-energy function suffices to govern the measured spectra; hence certain adiabatic and nonadiabatic effects must be either absent or negligible. We regard qualitatively the adiabatic effects to arise from the dependence of the potential energy on not only the internuclear distance but also the relative momenta of the nuclei, whereas the rotational and vibrational motions of the nuclei induce interactions with other electronic states that invoke the nonadiabatic effects. Because of the additional difficulty both to fit the spectra to the potential-energy coefficients and to regenerate the spectral lines from the latter parameters, and because the spectroscopist cannot be certain that the adiabatic and nonadiabatic effects are negligible, then to reduce the spectra merely to the term coefficients is practiced, thus to attain some desired compression of data (*3*) despite the lack of chemical or physical meaning of these term coefficients. Procedures of further reduction of these coefficients Y_{kl}, or more generally the subsets $Y_{k,0}$ and $Y_{k,1}$, to the potential-energy coefficients a_j in a separate successive process have been developed, for instance, with full statistical analysis based on analytic methods (*4*); by such means approximate functions for potential energy have been achieved but at the cost of either necessarily arbitrary selection of certain subsets of the term coefficients for the reduction or incorporation of all the term coefficients, even though there may exist possible inconsistencies within them due to a priori unknown adiabatic and nonadiabatic effects.

In the spirit of Dunham's analytic method, we have developed both a theory (*5*) and its implementation in an algorithm to enable the determination of all the feasible radial functions, potential energy and the composite adiabatic and nonadiabatic effects of each nucleus separately (in a heteronuclear diatomic molecule within an electronic state of type $^1\Sigma$), directly from the frequencies and wavenumbers of pure rotational and vibration–rotational transitions, of all applicable isotopic variants simultaneously. We have applied this procedure to relatively light molecular species such as the hydride LiH (*6*) and to more massive species such as the nonhydrides SiS (*7*), LiCl and LiBr (*8*); in each case spectral transitions involving molecules containing at least two variants of atomic nuclei of each kind were available. The separate determination of collectively the adiabatic and vibrational nonadiabatic effects and of (largely) the rotational nonadiabatic effects requires both that such isotopic diversity exists and that rotational excitation to a relatively large extent be attained in the set of measured transitions. Our experience with SiS (*7*), despite the diversity of its nuclidic variants, has indicated that, for relatively massive molecules and even for comparatively highly excited rotational states, the latter rotational nonadiabatic effects may be indeterminate. If the compound under investigation is composed of elements that lack stable isotopes, apart from the single massive stable nuclide of each atomic type, then one might hence be able to determine only the adiabatic potential-energy function; in these conditions the fitting procedure is accordingly simplified, as has been practised for many years (*4*).

The molecular species ^{27}Al^{19}F belongs to a compound for which nuclides of only one mass number for each atomic type are available. From accurate measurements of its abundant spectral lines (*9–11*), a data set became available that permits tests of fitting procedures; the data set includes 30 pure rotational transitions (*9, 10*) and 519 vibration–rotational transitions (*11*) extending up to $v = 5$. A previous measurement (*12*) of only 52 vibration–rotational lines of AlF up to only $v = 3$ was the basis of a fit of the combined rotational and vibration–rotational transitions directly to the potential-energy function in Eq. (2), although Niay *et al.* (*2*) achieved the first fit of vibration–rotational data to such an analytic function several years previously. Here we compare the reported results of the linear fit to the term coefficients Y_{kl} (*11*) with the results of the same parameters calculated from the potential-energy coefficients c_j that we determined from the same pure rotational and vibration–rotational transitions; for this reason we neglect the few lines of the earlier measurements (*12*) that were not duplicated in the larger set of data (*11*), but the precisions of measurement of the two sets (*11, 12*) of data are comparable. The coefficients c_j are factors of the reduced displacement variable $z = 2(R - R_e)/(R + R_e)$ according to the function (*13, 14*)

$$V(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j), \tag{3}$$

which lacks the serious problems of convergence that afflict Dunham's function of similar form because as $R \rightarrow \infty$, $x \rightarrow \infty$ but $z \rightarrow 2$.

By means of the same algorithm, in improved implementation, that we had used previously to determine the radial functions of several other diatomic molecular species (*6–8*), we have calculated the values of the potential-energy coefficients $c_j, j \leqslant 6$, and other spectral parameters of ^{27}Al^{19}F that suffice to reproduce the frequencies and wavenumbers of the known 30 pure rotational transitions (*9, 10*), up to $v = 4$ and $J = 11$, and 519 vibration–rotational transitions (*11*), up to $v = 5$ and $J = 91$. The standard deviation of the fit of the infrared transitions is 0.0460 m^{-1}; each (estimated) uncertainty associated with the parameters in Table I represents one standard error. The independent parameters number eight, the six potential-energy coefficients c_j, $1 \leqslant j \leqslant 6$, the harmonic force coefficient k_e, and the equilibrium internuclear separation R_e; the other parameters are directly related to these; for instance $U_{1,0} = (1000\, k_e N_a)^{1/2}/(2\pi c)$, $U_{0,1} = 1000\, hN_a/(8\pi^2 c R_e^2)$, *and* $c_0 = U_{1,0}^2/(4U_{0,1})$ with N_a, c, and h being the fundamental physical constants. Although we attempted to fit some coefficients g_j in an auxiliary radial function (*6*) to represent (mostly) the rotational adiabatic effects, we found that no such coefficients were determined significantly.

Having produced the values of these eight parameters, we readily calculated therefrom the values of the term coefficients Y_{kl} by direct substitution into the published analytic relations (*15*), specifically all those Y_{kl} that involve the potential-energy coefficients up to c_6 inclusive; the results appear in the first column of Table II. In accordance with the general dictum in science that *a numerical value which lacks an explicit estimate of its significance is worthless,* we sought to associate with each such value of Y_{kl} an uncertainty propagated ultimately from the measurements of frequency and wavenumber through the parameters in Table I. To take into account this propagation

TABLE I

Coefficients of the Radial Function $V(z)$ for Potential Energy and Other Molecular Parameters of $^{27}\mathrm{Al}^{19}\mathrm{F}\ X\ ^1\Sigma^+$

j	c_j	other parameters
0	29128865.15 ±9.2) m^{-1}	
1	-2.18344050 ±0.0000156	
2	2.7909594 ±0.000124	$U_{1,0}$ = (267890.725±0.049) $\mathrm{m}^{-1}\ \mathrm{u}^{1/2}$
3	-2.236162 ±0.0022	$U_{0,1}$ = (615.930625±0.000033) m^{-1} u
4	1.01410 ±0.0191	k_e = (422.83009±0.00029) N m^{-1}
5	-0.7038 ±0.094	R_e = (1.6543690±0.00000139)x10^{-10} m
6	1.538 ±0.72	

of error, two methods are available, that we describe as analytic and numerical. According to the former procedure (*4*), the variance–covariance matrix produced during the calculation of the uncertainties of the parameters in Table I is combined with the evaluation of analytic expressions of the partial derivatives of the coefficients Y_{kl} with respect to the coefficients c_j, etc., to produce the corresponding variance–covariance matrix of the latter parameters; this calculation naturally yields directly the estimated standard errors. According to the latter procedure (*16*), a calculation of Monte-Carlo type is performed many times with each parameter in Table I being varied within one standard error having as factor a random number of magnitude less than unity and generated according to a rectangular distribution; hence the covariance relations, or correlations between the input parameters, are taken implicitly into account in the resulting estimated uncertainties of the coefficients Y_{kl} (*16*). The mean values of the resulting coefficients Y_{kl} are presented with their standard errors in the second column of Table II. That agreement between the directly calculated values and the mean values of the coefficients in the first two columns is well within the stated uncertainties indicates both the numerical stability of the method and that 100 cycles suffice to produce statistically meaningful results. The values of potential-energy coefficients c_j calculated from the term coefficients $Y_{k,0}$ and $Y_{k,1}$ according to the iterative method developed many years ago (*4*) are essentially identical to those appearing in Table I; this agreement is further proof that nonadiabatic rotational effects are negligible within the range of the available spectral data and the measurement uncertainties, because this procedure (*4*) takes into account no centrifugal-distortion coefficients corresponding to the term coefficients corresponding to the term coefficients Y_{kl}, $l > 1$, which these nonadiabatic effects affect most perceptibly. The ratios of the estimated standard errors of the parameters Y_{kl} propagated from the potential-energy coefficients c_j in Table I according to the Monte-Carlo calculation to the corresponding estimated stan-

TABLE II

Comparison of Term Coefficients Y_{kl} from Different Methods of Spectral Reduction of Vibration-Rotational Data of AlF $X\ ^1\Sigma^+$

Coefficient	Exact/m^{-1}	Average Value/m^{-1}	Value[a]/m^{-1}
$Y_{0,0}$	18.7384	18.7383±0.0034	
$Y_{0,1}$	55.2480051	55.2480049±0.0000030	55.2480296±0.0000049
$Y_{0,2}/10^{-4}$	-1.0478740	$-1.0478740\pm4.9\mathrm{x}10^{-7}$	-1.048280±0.000068
$Y_{0,3}/10^{-11}$	-3.646156	-3.646139±0.00052	-3.050±0.093
$Y_{0,4}/10^{-16}$	-1.26332	-1.26335±0.00052	
$Y_{0,5}/10^{-23}$	-9.844	-9.820±0.20	
$Y_{0,6}/10^{-28}$	6.97	7.00±0.19	
$Y_{0,7}/10^{-33}$	5.68	5.66±0.25	
$Y_{0,8}/10^{-38}$	2.73	2.69±0.24	
$Y_{1,0}$	80232.3804	80232.3807±0.0047	80232.385±0.015
$Y_{1,1}$	-0.4984000	-0.4983997±0.0000031	-0.4984214±0.0000060
$Y_{1,2}/10^{-7}$	1.75558	1.75552±0.00124	1.8548±0.0080
$Y_{1,3}/10^{-12}$	1.0367	1.0376±0.0077	
$Y_{1,4}/10^{-18}$	6.843	6.857±0.129	
$Y_{1,5}/10^{-23}$	2.37	2.35±0.21	
$Y_{1,6}/10^{-29}$	3.64	3.26±3.1	
$Y_{2,0}$	-484.9497	-484.9500±0.0123	-484.9536±0.0098
$Y_{2,1}/10^{-3}$	1.70967	1.70992±0.00167	1.7153±0.0022
$Y_{2,2}/10^{-9}$	6.952	6.961±0.068	6.01±0.19
$Y_{2,3}/10^{-14}$	1.68	1.65±0.20	
$Y_{2,4}/10^{-20}$	-7.41	-7.95±4.7	
$Y_{3,0}$	1.9491	1.9497±0.0045	1.9497±0.0024
$Y_{3,1}/10^{-6}$	5.56	5.54±0.50	5.03±0.24
$Y_{3,2}/10^{-11}$	-5.4	-5.6±1.01	
$Y_{4,0}/10^{-3}$	-2.94	-2.99±0.68	-2.95±0.20

[a] reference 11.

dard errors propagated from the uncertainties of the subset of the coefficients Y_{kl} fitted from the transition frequencies and wavenumbers according to an analytic method vary within a range 0.5–2.0. Although some systematic trends in this ratio are discernible, such a range of variation is of no concern; the reason is that the analytic method takes explicitly into account the covariances (or correlation coefficients of the parameters) whereas the Monte-Carlo procedure makes no explicit use of the covariances of the coefficients c_j. There were reported (*11*) no covariances of the term coefficients Y_{kl} that are required to produce more accurate values of the variances of, and covariances among, the potential-energy coefficients c_j and correspondingly the correlation coefficients between the generated values of other term coefficients Y_{kl}.

In the final column of Table II appears the set of parameters that Hedderich and Bernath (*11*) fitted directly to the same set of 549 transitions (with the same statistical weights); we calculated the standard deviation of their fit to the infrared lines to be 0.0477 m^{-1}. The former authors fitted the data to twelve nominally independent coefficients Y_{kl}; that of highest order, $Y_{4,0}$, implies the coefficient c_6 of maximum degree in the potential-energy function that we determined. The latter degree of the potential-energy function implies however 12 further coefficients Y_{kl} that could not be determined directly during the fit of the spectral transitions, in addition to $Y_{0,0}$ which cannot be determined directly. As the magnitude of the smallest determined coefficient (*11*), $Y_{0,3} \sim 4 \times 10^{-11}\ \mathrm{m}^{-1}$, is however comparable with the magnitude of the largest further coefficient, $Y_{3,2} \sim 5 \times 10^{-11}\ \mathrm{m}^{-1}$, of which the magnitude of the associated standard error is also comparable, and as all further coefficients had significantly smaller magnitudes even if (in most cases) relatively small errors, no advantage would have been derived from the inclusion of these coefficients in the fitting model. The standard errors of most coefficients Y_{kl} determined from the direct fit exceed greatly the errors propagated from the potential-energy parameters; in the cases of $Y_{3,0}$, $Y_{3,1}$, and $Y_{4,0}$, the propagated standard errors exceed significantly those from the direct fit. The former effect we attribute to the implicit truncation of the fitting model, for instance, of the series $Y_{k,3}$ at $Y_{0,3}$ and $Y_{\mathrm{k},2}$ at $Y_{2,2}$. The agreement of the coefficients Y_{kl} between the direct fit and our indirect calculation is generally within two standard errors, except in those cases sensitive to the truncation just described. That the discrepancies are generally negligible is consistent with our failure to determine any coefficients of the radial function for the rotational adiabatic effects which had previously been found to cause such discrepancies. The absence of these effects in AlF is consistent with our findings for SiS (*7*), for which rotational excitation to a much greater extent was measured (*17–19*).

In conclusion we have confirmed that for AlF the careful fit (*11*) of the term coefficients directly to pure rotational (*9, 10*) and vibration–rotational transitions (*11*) produces values of Y_{kl} almost indistinguishable from those generated indirectly from the potential-energy coefficients, although both the standard deviation of the fit and the standard errors of most coefficients Y_{kl} are larger in the former procedure (*11*) than those produced in the direct fit to the potential-energy function. As the latter procedure not only required fewer parameters, eight compared with 12, but also produced a physically meaningful function, namely, the radial dependence of the potential energy which is a fundamental molecular property of the particular electronic state $X\,{}^1\Sigma^+$ of AlF, instead of a set of mere fitting parameters (*2*), our contention (*3*) that the latter procedure is generally preferable is confirmed. The reproduction of the transition frequencies and wavenumbers directly from the potential-energy coefficients c_j, B_e, and ω_e poses no complicated computations (such as the numerical solution of differential equations) because the expressions (*15*) relating these parameters (up to at least c_6) to the term coefficients Y_{kl} are sufficiently simple to be evaluated on a suitable programmable pocket calculator. The potential-energy function that we generated for AlF $X\,{}^1\Sigma^+$ is valid in the approximate range of internuclear distance $1.48 < R/10^{-10}\ \mathrm{m} < 1.91$, and the uncertainties of k_e and R_e in Table I take into account the standard errors of the fundamental physical constants h and N_a.

ACKNOWLEDGMENTS

We thank the National Science Council of the Republic of China for support of this research, and Professor P. F. Bernath for kindly supplying data before publication.

RECEIVED: January 29, 1992

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