Inversion of Polyatomic Rovibration Spectra into a Molecular Potential Energy Surface: Application to CO_2

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The experimental vibrational energies for the stretching modes of the CO_2 molecule are used, with a recently developed method for generalizing the Rydberg-Klein-Rees inversion technique to polyatomics, to obtain a two-dimensional potential surface for nonbending CO_2. The resulting surface appears quite accurate; this demonstrates the ability of the method to obtain actual polyatomic potential surfaces and constitutes the first successful determination of a polyatomic potential surface by inversion of spectra.

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The method of choice for obtaining diatomic potential energy surfaces is the inversion method developed by Rydberg, Klein, and Rees (RKR).[1] In a previous publication[2] we suggested a method for extending the inversion to polyatomic molecules, and tested it on a model system of two coupled oscillators. In this Letter we present results of an inversion of spectroscopic data for $^{12}C^{16}O_2$.

The RKR inversion is performed by obtaining the values of f and g for each available spectroscopic state, where f and g are experimental quantities defined as

$$f=(\hbar^2/2\mu)^{1/2}\int_{-1/2}^{n}(E_n-E_{n'})^{-1/2}\,dn', \quad g=(2\mu/\hbar^2)^{1/2}\int_{-1/2}^{n}B_n(E_n-E_{n'})^{-1/2}\,dn',$$

with the experimental vibrational/rotational energy dependence given by

$$E_{n'}=\omega_e(n'+\tfrac{1}{2})-\omega x_e(n'+\tfrac{1}{2})^2+\omega y_e(n'+\tfrac{1}{2})^3+B_eJ(J+1)-\alpha_eJ(J+1)(n'+\tfrac{1}{2})-D_eJ^2(J+1)^2+\dots .$$

The values of f and g are then related to the classical turning points X_r and X_l by

$$f=\tfrac{1}{2}(X_r-X_l), \quad g=\tfrac{1}{2}(1/X_l-1/X_r).$$

A plot of the energy levels versus the corresponding turning points forms the potential.

Since the RKR inversion is based on the WKB approximation, which applies only in one dimension, it cannot be directly extended to polyatomic molecules. We get around this problem by basing our method on the self-consistent-field theory (SCF) for molecular vibrations. In this way we define separable vibrational modes on which to perform one-dimensional inversions. These inversions create sets of single-mode SCF potentials from which we obtain the multidimensional potential surface.

The SCF procedure for coupled vibrational systems has been defined and tested by Bowman[3] and Kern[4] and their collaborators. We have shown[5] that the SCF procedure can be simplified by replacing the quantum matrix elements by their semiclassical equivalents, resulting in the semiclassical SCF method (SC-SCF).[5] It is the SC-SCF that underlies our extension of the RKR inversion to polyatomic molecules. We will here briefly develop the polyatomic inversion method and then apply it to the bending vibrations of CO_2.[6] The resulting two-dimensional potential surface is equivalent to the cut in the full potential at the equilibrium bending angle of 180°. This potential is compared to the same cut in a very elaborate fitted surface.

The inversion is defined in a set of coordinates chosen such that the kinetic energy is diagonal. The potential may then be described as a sum of single-mode terms and a coupling term:

$$W(q_1,q_2)=V_1(q_1)+V_2(q_2)+V_{12}(q_1,q_2).$$

The SC-SCF theory is based on obtaining single-mode energies from a set of coupled equations of the form (for mode 1)

$$\int_{q_{1l}}^{q_{1r}} \{[E_1^{(m,n)} - U_1^{(n)}(q_1)]2\mu_1\}^{1/2} dq_1 = (m+\tfrac{1}{2})\pi h, \tag{1}$$

where m and n are the quantum numbers in modes 1 and 2, respectively, $E_1^{(m,n)}$ is the single-mode energy in mode 1 which is dependent on both m and n, μ_1 is the reduced mass, $U_1^{(n)}$ is the effective potential defined as

$$U_1^{(n)}(q_1) = V_1(q_1) + \int_{q_{2l}}^{q_{2r}} [V_{12}(q_1,q_2)/P_2^{(m,n)}(q_2)]dq_2, \tag{2}$$

$P_2^{(m,n)}$ is the momentum in mode 2, and q_{1r}, q_{1l}, q_{2r}, and q_{2l} are turning points of $U_1^{(n)}$ and $U_2^{(m)}$, respectively. Equation (1) is simply the SCF extension of the Bohr-Sommerfeld quantization condition. Since the RKR inversion is derived from the Bohr-Sommerfeld quantization, Eq. (1) and its analog for mode 2 can be inverted in a similar manner to give, f_1, g_1, f_2, and g_2 for each available energy level. These f and g values can then be related to the turning points to give $U_1^{(n)}$ and $U_2^{(m)}$ for all available n and m.

To complete the inversion we must obtain V_1, V_2, and V_{12} from the U's. This is done, for mode 1, by extrapolating the $U_1^{(n)}$, available for $n = 0, 1, 2, \ldots$, to $n = -\frac{1}{2}$. At $n = -\frac{1}{2}$ the turning points in mode 2 are equal, $q_{2r} = q_{2l}$, and from Eq. (2) we can define

$$U_1^{(n=-1/2)}(q_1) = V_1(q_1).$$

V_2 can be obtained similarly. Rewritting Eq. (2) as

$$\int_{q_{2l}}^{q_{2r}} \frac{V_{12}(q_1,q_2)}{P_2^{(m,n)}(q_2)} dq_2 = U_1^{(n)}(q_1) - V_1(q_1),$$

one sees that the right-hand side is now available for all values of q_1 and n; a systematic numerical procedure for solving for V_{12} can then be given.[7] With V_1, V_2, V_{12} available, the inversion is complete.

Our primary reasons for choosing CO_2 as a first application of the inversion are twofold: First, the completeness and accuracy of the overtone spec-

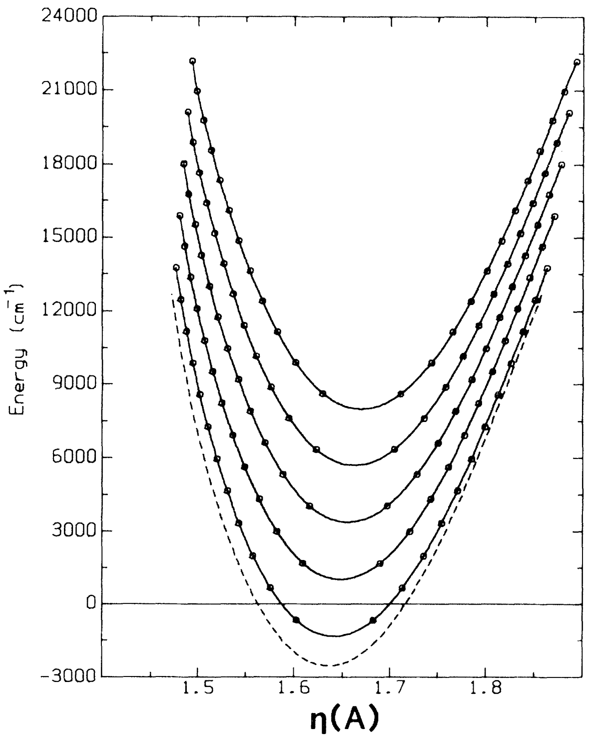

FIG. 1. The effective potential $U_1^{(n)}$ along the η coordinate for $n = 0, 1, 2, 3, 4$ (solid lines), and the bare potential $V_1 = U_1^{(n=-1/2)}$ (dashed line).

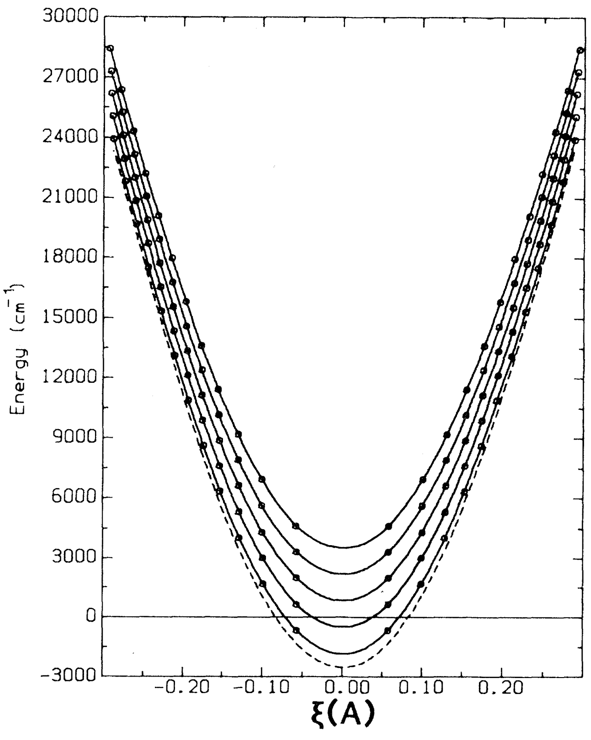

FIG. 2. As in Fig. 1, but for mode 2 along the ξ coordinate.

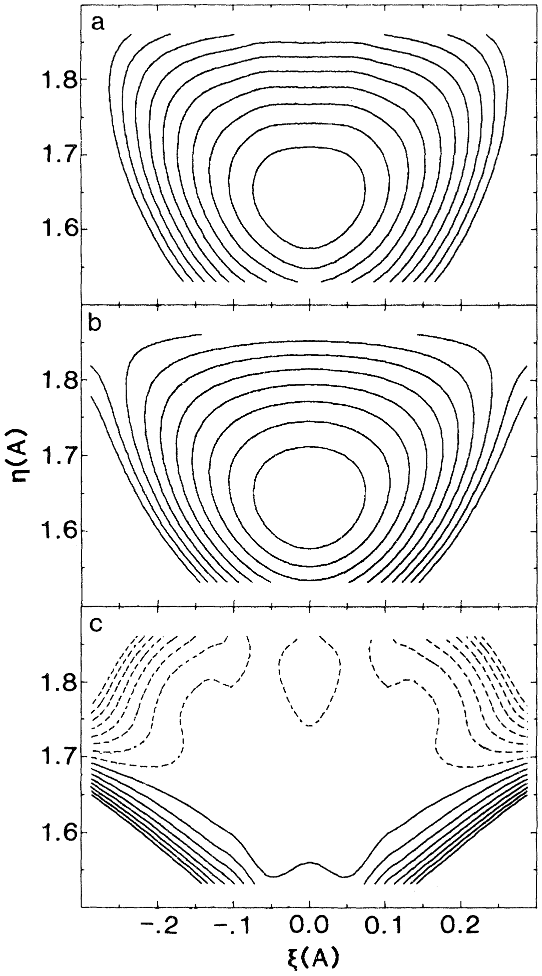

FIG. 3. The cut of the full potential at bending angle of 180°. (a) The potential from inversion. (b) The potential from Ref. 10. The contour levels are 2000 cm^{-1}. (c) The difference between (a) and (b), contours between $\pm 3000\ \text{cm}^{-1}$ with 400-cm^{-1} increments.

trum of CO_2 is excellent[8]; and second, the symmetry of the potential surface simplifies the inversion procedure. In order to keep this problem tractable, we have only inverted the two-dimensional cut of the surface at its equilibrium bending angle of 180°. This two-dimensional cut of the potential represents the first step in obtaining the full surface in three coordinates, and produces (Fig. 3) contour diagrams which are both easily interpreted and straightforwardly compared to experiment.

The coordinate system used for the inversion, in terms of the internal C-O stretching displacements r_1 and r_2, is

$$\eta = (r_1 + r_2)/\sqrt{2}, \quad \xi = (r_1 - r_2)/\sqrt{2}.$$

These are simply the normal-mode coordinates, symmetric and antisymmetric, respectively. Any single-mode potential must be symmetric in ξ, constraining its turning points such that $\xi_r = -\xi_l$. This symmetry relation simplifies the inversion procedure by requiring only three turning points to be obtained from the f and g values.

The energy values used in the inversion are obtained from very accurately fitted spectroscopic constants (ω's, x's, y's, α's, γ's, ...).[9] This allows us not only to freeze out the (degenerate) bend by placing its quantum number at -1, but also to exclude the effects of Fermi resonance.

Some of the resulting single-mode effective potentials, U's, along with the bare single-mode potentials, V's, are given in Figs. 1 and 2. The two-dimensional potential is shown in Fig. 3, and is compared with a potential surface previously derived[9] by trial-and-error-fitting to the same numerical data. We also show the difference between the two. We observe that the inverted surface agrees closely with the fitted surface near the axes of the normal displacement coordinates ($\eta = 1.64$ Å, $\xi = 0.0$ Å). Further away from the axes the deviations become larger. Since the near-axes region is weighted heavily in the fitted potential,[9] these large deviations are not surprising. The dissociation properties of the inverted potential appear better than the fitted one.

Further tests of our inverted potential by computation of observable properties such as intensities will be given elsewhere.[10] We feel that the success of the SC-SCF/RKR inversion procedure in obtaining the potential of Fig. 3 is a promising step towards its general application in finding potentials from vibrational data. As an inversion scheme, the method avoids the arbitrariness of trial-and-error fitting, and provides better insight into the relation between potential and data. Thus, the RKR/SCF method may become important for obtaining molecular potential energy surfaces.

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[6] For simplicity, the equations in this brief development have the rotational quantum number J set equal to zero so that the rotational terms vanish.

[7] This integral is similar to the Riemann-Stieltjes integral for which numerical solutions are well known; see T. M. Apostol, *Mathematical Analysis* (Addison-Wesley, Reading, Mass., 1957), p. 200; R. M. Roth, M. A. Ratner, and R. B. Gerber, to be published.

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[10] Both the computation of the full surface (inclusion of the bend) and the intensity calculation require slight extension of the simple formalism given here, and will be described elsewhere.