**Ab initio synthesis of the ozone ultraviolet continuum**

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(Received 23 September 1986; accepted 9 February 1987)

Potential energy surfaces for the ground and excited electronic states responsible for the Hartley continuum of ozone are used to obtain quadratic, cubic, and quartic force constants. Vibrational dependence of rotational constants to sixth order is calculated by perturbation theory. The spectroscopic constants enable computation of rovibrionic energy levels. Overlap of ground state and excited state perturbed vibrational wave functions yield Franck–Condon factors. Electric dipole allowed rovibronic transitions are generated under the \( I' \) representation. The entire set of results generate the ultraviolet absorption spectrum. It is shown that inclusion of anharmonic terms in the vibrational Hamiltonian has a small effect upon the final spectrum, whereas rotational broadening plays a greater role in achieving agreement with experiment.

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**INTRODUCTION**

The ozone molecule continues to be of interest to theoretician and experimentalist.\(^{1–7}\) This is due to its importance in atmospheric chemistry and physics, and its amenability to \textit{ab initio} calculations.\(^{8–10}\) It seemed to us that an improvement in theoretical band shapes is possible if several features normally disregarded for polyatomic systems were accounted for. These include transitions from discrete, Boltzmann-populated vibrational levels, anharmonic effects in a Franck–Condon spectral synthesis, and rotational fine structure.

In a recent article\(^{11}\) the fact was expressed that certain features of absorption spectra are unique to polyatomic systems, including the vibrational structure of an electronic transition to a dissociative state.\(^{12–14}\) This applies to ozone, in which the \( C_2 \) dissociation pathway results in formation of diatomic oxygen which exists in a multitude of rovibrionic states. Thus, our work may test such a concept on a system of interest. A word of caution in interpreting our results: It is completely nonempirical, making it difficult to compare with our calculations based upon fittings to spectral data. To our knowledge, this is the first such \textit{ab initio} spectral synthesis for a polyatomic system.

Many studies have been concerned with the electronic states of ozone,\(^{15–17}\) and a number of workers have performed studies of the ground-state potential energy surface.\(^{17–21}\) The ground state of ozone has the experimental equilibrium geometry listed in Table I, while the excited \( ^1B_2 \) state responsible for the Hartley continuum is believed to have a \( (C_2v) \) bond length of 2.655 bohr with a bond angle of 108°. This surface is inherently dissociative and correlates with the fragments \( O_2(\Delta_g) + O(\Delta_D) \).

Hay and Dunning have performed \textit{ab initio} calculations for several electronic states of ozone.\(^{15}\) Hay, Pack, Walker, and Heller generated spectra out of the (000) level using the Gaussian wave packet method.\(^{22}\) Sheppard and Walker used the classical Wigner method to obtain ultraviolet spectra out of vibrationally excited ozone.\(^{23}\) They employed both \textit{ab initio} and empirically adapted surfaces, parametrized as outlined below.

Adler–Golden has also contributed an interesting study of ozone absorption.\(^{24}\) In this work, a Franck–Condon spectral synthesis generated the ultraviolet continuum, over a wide temperature range. Agreement with experiment (\( CO_2 \) laser vibrationally excited ozone) is good, and a semiempirical expression is given for temperature-dependent ozone UV absorption.

This article presents the theory behind our generation of the spectrum. All spectroscopic constants are obtained in the process. The final section is a tabulation and discussion of our results.

**THEORY**

The current work proceeds from the \textit{ab initio} results of Hay and Dunning, together with the parametrization of Sheppard and Walker.\(^{15,22,23}\) Hence, we give details of this previous work first. Hay, Pack, Walker, and Heller performed the calculation of the \textit{ab initio} potential energy surfaces which we employ. The GVB-PP (perfect-pairing) MCSCF technique was used in conjunction with a \( (3s2p1d) \) contracted Gaussian basis set for all surfaces. This was done over a grid of points described by \( 95° < \alpha < 135° \), \( 2.1 < r_1 < 10.0 \) bohr, \( 1.9 < r_2 < 3.1 \) bohr, with \( r_2 < r_1 \).

The authors\(^{22,23}\) decided to fit their calculated surfaces...
to an analytic form, and chose that of Murrell, Sorbie, and Varandas, with details given below. As the authors state the accuracy of these $X(1A_1)$ and $B(1B_2)$ surfaces may be described by the number of points $(N)$ and rms error $(\sigma)$: $X(N=93), \sigma = (0.02 \text{ eV}), B(N=93, \sigma = 0.06 \text{ eV})$. Shepard and Walker parametrized the $ab\ initio$ surfaces calculated by Hay and Dunning as the sum of two-body and three-body terms:

$$V_{2B} = -D \sum X \left(1 + \beta X + \gamma X^2 + \delta X^3\right),$$

$$V_{3B} = \left[1 - \tanh(\Gamma q_i)\right] \sum_{i=0}^{30} c_i p_i(q_1, q_2, q_3).$$

The term $V_{2B}$ represents the potential contributed by the three pairs of oxygen atoms (given the form of an extended Morse potential), where $x_i = r_i - R_0$ for $i = 1, 3$ is the displacement from the diatomic equilibrium separation $r_0$ and $D$ is the dissociation energy in eV. The term $V_{3B}$ represents the potential energy which cannot be accounted for by consideration of pair interactions and vanishes if any atom approaches infinite separation from the remaining two. Here $\Gamma$ is a constant (for a given surface) which yields the correct asymptotic behavior, while $q_1$, $q_2$, and $q_3$ are external symmetry coordinates defined by

$$q_1 = \frac{1}{\sqrt{3}} \left( r_1 + r_1 + r_3 - R_0 \right),$$

$$q_2 = \frac{1}{\sqrt{2}} \left( r_2 - r_3 \right),$$

$$q_3 = \frac{1}{\sqrt{6}} \left( r_1 - \frac{1}{3} (r_2 + r_3) \right)$$

($R_0$ is a constant for a given surface) and $p_i$ are polynomials of the form $q_i b_m c_n$, where $b_2 = q_2^2 + q_3^2$, $c_1 = q_1(q_3^2 - 3q_2^2)$, and $0 < l + m + n < 7$. Values for the coefficients $c_i$ are in the appendix of Shepard and Walker’s paper; we have used the set based on $ab\ initio$ diatomic curves.

Some key parameters for these surfaces are as follows. The vertical excitation energy from the $1A_1$ ground state, along the $C_2$ axis, or $1.53 \text{ eV}$ above the saddle point on the $1B_2$ surface, plus the $555$ lowest lying states of $1B_2$ ozone; for the latter (4) is replaced by a sum of double products as we are considering only the nondissociative modes $Q_1$ and $Q_2$ at this stage. The number of $1B_2$ vibrational states was based upon considerations of the Los Alamos surface, and reflects the semiclassical nature of the wave function amplitude for large values of $v_1$ and $v_2$.

We devised a computer program to compute all derivatives to fourth order with respect to the internuclear separations $r_1$, $r_2$, and $r_3$ at any given geometry for both ground and excited ($1B_2$) states. To determine harmonic frequencies and anharmonic constants we converted to normal coordinates $Q_1$, $Q_2$, and $Q_3$ for the three vibrational modes $v_1$ (symmetrical stretch), $v_2$ (angle bend), and $v_3$ (asymmetrical stretch). This was done via the internal symmetry coordinates defined as

$$q_k = \frac{1}{\sqrt{2}} \left( r_2 + r_3 \right),$$

$$q_i = r_2(\alpha - \alpha_e),$$

$$q_m = \frac{1}{\sqrt{2}} \left( r_2 - r_3 \right).$$

Here note that $r_2$ and $r_3$ are the bonded internuclear distances, while $r_1$ is the nonbonded distance. Such a transformation of derivatives through fourth order was nontrivial, and involved the evaluation of dozens of terms based on the Jacobian $\partial(q_1, q_2, q_3)/\partial(r_1, r_2, r_3)$. The calculations were performed by the program. The $L$ matrix which converts symmetry adapted to normal coordinates was found by standard GF matrix formalism, obtaining enroute the zeta-matrix elements for both electronic states. Let $z$ be the $C_2$ axis and $x$ be perpendicular to the molecular plane. Using this choice of axes (known simply as the $I^\prime$ representation), only the $3 \times 3$ matrix is nonzero, as

$$\xi = \begin{pmatrix} c_1 & c_2 & c_3 \\ c_2 & c_4 & c_5 \\ c_3 & c_5 & c_6 \end{pmatrix}.$$

Having thus arrived at a listing of all force constants to fourth order, one seeks to determine how the vibrational wave functions, being harmonic oscillator (HO) functions in zeroth order, are perturbed by the presence of six cubic force constants and six quartic constants. Using first order perturbation theory one writes

$$\psi_{ik}^{(0)} = \frac{1}{\sqrt{2}} \left( E_i - E_k \right) \psi_{ik}^{(0)} ,$$

where $\psi_{ik}^{(0)}$ is a triple product of HO wave functions $\psi_{ij}^{(0)}$, $\psi_{ik}^{(0)}$, $\psi_{jk}^{(0)}$ is the anharmonic Hamiltonian operator, and $\psi_{ik}^{(0)}$ is the corrected function. Such an algorithm was devised for the 20 lowest-lying states of $1A_1$ zone, plus the 555 lowest lying states of $1B_2$ ozone; for the latter (4) is replaced by a sum of double products as we are considering only the nondissociative modes $Q_1$ and $Q_2$ at this stage. The number of $1B_2$ vibrational states was based upon considerations of the Los Alamos surface, and reflects the semiclassical nature of the wave function amplitude for large values of $v_1$ and $v_2$. In fact, a subsidiary program was needed to calculate all Hermite polynomials to order 50. The evaluation of Eq. (4) above was performed numerically using the Romberg method to derive Cotes sums over a grid of points broad enough that the exponential factor in $H_\alpha(\chi)$ had decayed to at least $e^{-4}$, thereby ensuring sufficient coverage for the integration procedure. This was a triple integration; the three-dimensional $[q_1, q_2, q_3]$ surface was summed over with a set of approximately one-third million points. A comparison of the vibrational energies obtained using this perturbation approach to experiment and to energies obtained by others using variational methods is given in the next section.

The perturbed vibrational wave functions are first used to find the vibrational dependence of the three rotational constants $B_x$, $B_y$, $B_z$. Here

$$\frac{1}{r_{ik}} = \left. \frac{1}{\psi_{ik}^{(1)}} \right| \frac{1}{\psi_{ik}^{(0)}} \psi_{ik}^{(1)}$$

and

$$\frac{1}{\alpha_{ik}} = \left. \frac{1}{\psi_{ik}^{(1)}} \right| \frac{1}{\psi_{ik}^{(0)}} \psi_{ik}^{(1)},$$

where $\psi_{ik}^{(1)}$ is the corrected (perturbed) wave function for either electronic state.
Care must be exercised in recovering $r_i$ from this expression, as we are in normal coordinates. The success of the above was evident in a smooth, quasilinear variation of the rotational constants with increasing vibrational quantum number, in accord with the experimental result that

$$B_k^v = B_k^{v0} - \sum \alpha_k^n (v + \frac{1}{2}).$$  \hspace{1cm} (7)

Here $v$ is the vibrational quantum number and $k = x, y, z$ ($I^r$ rep.).

Using standard formulas\textsuperscript{26} one easily computes the vibrational level energies in cm$^{-1}$, given the harmonic frequencies and anharmonic constants. Any levels closer than 50 cm$^{-1}$ were then recorrected due to Darling–Dennison resonance, employing $\gamma$ calculated from the data. In truth such a resonance exists between the (200) and (002) levels of ground state ozone.\textsuperscript{27}

Having found the vibrational band origins we calculate the higher order rotational constants starting with the $B_k$ above. The theory employed is that of contact transformations,\textsuperscript{28} leading to the result that the vibrational–rotational Hamiltonian is just $H = \Sigma_{m,n} H_{mn}$, where $m$ refers to the degree of the vibrational operators and $n$ to the degree of the components of the angular momentum operator $J$.

Considering more specifically the pure rotational Hamiltonian, using the notation of Watson\textsuperscript{29} one has

$$H^{rot} = \sum_{p,q,r = 0} h_{pq} (J_p J_q + J_q J_p),$$  \hspace{1cm} (8)

$h_{pq}$ being a constant. The expression is written as is because it should be Hermitian. We wish to apply a unitary transformation to the given Hamiltonian in such a fashion that its general form remains the same, yet with new coefficients. We write $H = U^{-1}HU$, where $U$ is one such unitary transformation. Selecting the form $U = e^{S}$ is convenient, as it requires only that $S$ be Hermitian. We may separate $S$ and thereby factor $U$ as

$$U = e^{S_1}e^{S_2}e^{S_3} \ldots ,$$  \hspace{1cm} (9)

where $S$ has only terms such that $p + q + r = n$. The important result is that for any given order of the rotational Hamiltonian, the terms off-diagonal are removed to the next higher order, allowing for the determination of formulas for the quartic, sextic, etc., constants.

With this background, the quartic and sextic centrifugal distortion coefficients are determined as follows. Inertial defined as $a_i^q = (\partial I_{ij} / \partial Q_k)_{+}$ (a.u.) are used to find rotational derivatives, defined as

$$B_k^q = B_k^{q0} - (\alpha_i^q / 2h \alpha^{3/2} \omega^{1/2}) (a_i^q / I_a I_B).$$  \hspace{1cm} (10)

Here $I_{ij}$ is an element of the inertia tensor and $Q_k$ is a normal mode. Due to symmetry considerations it turns out that there are only six nonzero $B_k^q$. Finally one has $\tau_{odd} = -2 \Sigma B_k^q B_k^q \omega / \omega_k$ for the quartic centrifugal distortion coefficients. One converts these to “primed” coefficients by $\tau_{aodd} = \tau_{aaodd} = \tau_{aodd} + 2\tau_{odd}$, and uses these to find the empirical constants $\Delta_j, \Delta_{jk}, \Delta_{k},$ etc., as linear combinations of the $\tau_{aodd}$. Again the $J$ representation is used. The appropriate expressions are given in the appendix of Kivelson and Wilson's paper.\textsuperscript{30}

The computation of rotational energy levels is made simpler by initial transformation of the rotational Hamiltonian to cylindrical tensor form\textsuperscript{28}:

$$H^{rot} = H^{C2} + H^{C4} + H^{C6} = (B_{200} \tilde{J}_z^2 + B_{202} \tilde{J}_z^2 + T_{400} \tilde{J}_2^2 + T_{220} \tilde{J}_2^2 + T_{040} \tilde{J}_2^2 + \Phi_{600} \tilde{J}_z^3)$$

$$+ \Phi_{220} \tilde{J}_z^2 \tilde{J}_2^2 + \Phi_{204} \tilde{J}_z^2 \tilde{J}_2^2 + \Phi_{006} \tilde{J}_2^3 + \frac{1}{2} \left[ (B_{002} + T_{202} \tilde{J}_z^2 + T_{202} \tilde{J}_z^2 + T_{022} \tilde{J}_z^2 + \Phi_{022} \tilde{J}_z^2 + \Phi_{220} \tilde{J}_z^2 + \Phi_{042} \tilde{J}_z^2 + \Phi_{006} \tilde{J}_z^3) \right]$$

$$+ \frac{1}{2} \left[ (T_{024} + \Phi_{204} \tilde{J}_z^2 + \Phi_{024} \tilde{J}_z^2), \tilde{J}_2^2 \tilde{J}_z^2 + \Phi_{042} \tilde{J}_z^2 \tilde{J}_2^2 + \Phi_{202} \tilde{J}_2^2 \tilde{J}_z^2 + \Phi_{006} \tilde{J}_2^3 \right],$$  \hspace{1cm} (11)

where $[\bar{P},\bar{Q}]_+ = \bar{PQ} + \bar{QP}$ (anticommutator), and $\tilde{J}_z = \tilde{J}_z + i\tilde{J}_z$. Due to the presence of arbitrary parameters in Eq. (11), certain assumptions are usually made. In the “$A'$” reduction, one sets $T_{004} = \Phi_{204} = \Phi_{024} = \Phi_{006} = 0$. One then obtains a form for the Hamiltonian in which the diagonal elements are given by

$$E_{kk} = \langle J, K | H^{C(A)} | J, K \rangle = \frac{1}{2} \left[ (B_x + B_y) (J + 1) + \{B_z - \delta (B_x + B_y)\} K^2 - \Delta K J^2 (J + 1)^2 \right.$$

$$- \Delta K J (J + 1) K^2 - \Delta K K^4 + \Phi_{J} J^3 (J + 1)^3 + \Phi_{J K} J^2 (J + 1)^2 K^2 + \Phi_{K J} J (J + 1) K^4 + \Phi_{K} K^6 \right)^{1/2},$$  \hspace{1cm} (12)

and off-diagonal elements are simply\textsuperscript{28}

$$E_{K, K' \pm 2} = \langle J, K \pm 2 | H^{C(A)} | J, K' \rangle = \frac{1}{2} \left\{ J^\dagger (B_x - B_y) - \delta J (J + 1) + i \sigma K \right\} \{ (K \pm 2)^2 + K^2 \}$$

$$+ \frac{1}{2} \phi_{JK} \times J (J + 1) \{ (K \pm 2)^2 + K^2 \} \left[ (K \pm 2)^2 + K^4 \right] \times \left\{ J (J + 1) \right.$$

$$- K (K \pm 1) \right\} (J + 1) - K (K \pm 1) (K + 1) (K + 2)^2)$$. \hspace{1cm} (13)

Here the superscript “$A'$” refers to the $A'$ reduction, while the relations between the coefficients in Eqs. (12) and (13) to those in Eq. (11) have been given.\textsuperscript{28}

Recall that ozone, with an asymmetry parameter $\kappa = -0.968$, is a nearly prolate asymmetric top, for which there are $2J + 1$ values of $K_{-1}$ ranging from $-J$ to $J$. Thus one must diagonalize a set of matrices, $J_{\max}$ in number, of increasing size up to $(2J_{\max} + 1) \times (2J_{\max} + 1)$. Fortunately, each $J$ block may be factored into a $K_{-1}$-even and a $K_{-1}$-odd subblock.\textsuperscript{31} Figure 1 reveals that these subblocks are in simple tridiagonal form, and hence the complete eigensystem is solved by any subroutine which diagonalizes tridiagonal real, symmetric (Hermitian) matrices. In the actual program, the diagonal elements are components of a vector of dimension $\Sigma_{J=0}^\infty (2J + 1)^2$, and the off-diagonal elements are placed in a similar vector of dimension $\Sigma_{J=0}^\infty (2J + 1)$. The eigen-
values are returned to the original vector and added to the vibrational energies.

For $^{16}$O$_3$ the only allowed rovibronic levels are those of $A_1$ and $A_2$ permutation-inversion (PI) symmetry, where the PI group is isomorphic with the point group $C_{2v}$. Figure 2 shows the construction of these from electronic, vibrational, and rotational factors as well as the allowed electric dipole transitions, namely vibrations. 32 The anharmonic force fields effect upon band structure, one cannot use standard formulas for the overlap of electronic wave functions occurs slightly above the barrier top, corresponding to a positive kinetic energy needed to form fragments. The final program receives input from all prior programs (vibrational energies, rotational levels, overlap integrals, etc.) and generates an absorption spectrum assuming a constant electronic factor and a Boltzmann population of all ground rovibronic states. The assumption of a constant factor for the overlap of electronic wave functions was for the sake of computational tractability. In addition Hay and Dunning15 have calculated a transition dipole moment for the $^1B_2-^1A_1$ transition, and this is the factor used in our work. Note that anharmonic effects are made manifest in at least two ways: spacing of vibrational levels and magnitude of overlap integrals. The output is stored in 1 cm$^{-1}$ wide energy bins across the spectral region 0–50 000 cm$^{-1}$.

RESULTS AND DISCUSSION

Table I lists harmonic frequencies for the two electronic states $^1A_1$ and $^1B_2$ together with vibrational fundamentals for the state $^1A_1$. Also given are the equilibrium geometries for both electronic states, obtained by setting all first partial derivatives equal to zero for the surfaces employed. These values are accurate to 0.001 bohr and 0.05° for the bond distance and bond angle, respectively. Comparison of the ground-state equilibrium geometry with the experimental geometry indicates that the ground surface is quite accurate for our purposes. However, the authors22 state that the rms error for their excited state is three times greater than for the ground state. Thus, although the ground state $\omega_3$, $\omega_2$, $\omega_1$ are roughly within $\pm$ 6% of experiment (with $\omega_3$ being fortuitously close and with $\omega_1$ being too large and in the worst harmonic oscillator. The Schrödinger equation for a harmonic barrier may be brought into the simplified form $x'' + (ax^2 + b)x = 0$. Assuming a power-series solution of the form $x = \Sigma_{n=0}^\infty c_n x^n$ one obtains two independent solutions which are essentially the parabolic cylinder functions. The three-term recursion formula we have derived is $c_{n+4} = - (ac_n + bc_{n+2})/[(n+3)(n+4)]$. The power series obtained is convergent for reasonable values of coordinate $x$ ($Q_1$ in a.u.) only upon going to the 50th or 60th power. However, our solutions do give the physically reasonable result that the wave function behaves as indicated in Fig. 3, for various heights above and below the top of the barrier. It turned out that the greatest amount of overlap with ground state wave functions occurs slightly above the barrier top, corresponding to a positive kinetic energy needed to form fragments.

FIG. 1. Factoring of $J = 3$ matrix into $K_{-1}$ odd and even subblocks. Circles are diagonal elements, crosses off-diagonal.

FIG. 2. Pattern of electronic, vibrational, and rotational components of rovibronic states connected by the electric dipole operator $\mu_x$ which transforms as the $A_1$ irreducible representation of the permutation-inversion group for $^{16}$O$_3$.
agreement), the values for the excited state may be of less certainty.

Listed in Table II are calculated quadratic, cubic, and quartic force constants, plus the ground-state values obtained by the usual spectroscopic fitting procedure. The calculated values for the ground-state cubic constants correctly predict both the relative size of these constants, and in most cases are accurate within ±15%. Such agreement is also predicted for the excited state cubic constants, except for the relative crudity of this surface. In contrast the ground-state quartic force constants agree only in order of magnitude with spectroscopic data, and sometimes even the wrong sign is predicted. However, the large value of \( k_{133} \) is still apparent in the \textit{ab initio} data, as well as some remarkably close agreements for some of the other constants.

Figure 4 displays the effect of anharmonic terms upon calculated vibrational levels for the ground state. The results of our perturbation treatment bring the levels into closer agreement with experiment \(^{1(5)} \) than otherwise. Overall, the level of agreement is satisfactory, although with the computed fundamental \( v_1 \) being 97 cm\(^{-1} \) too large (Table I), the overtone (200) and the combinations (110) and (101) are also too large, by 213, 90, and 88 cm\(^{-1} \), respectively. The overtones (020) and (002) are 44 and 10 cm\(^{-1} \) too low, respectively, while the combination (011) is only 8 cm\(^{-1} \) too low. The recent variational calculations \(^{21(b)} \) of Adler-Gorden et al. using a CASSCF/DZP \textit{ab initio} surface yielded fundamentals, overtones, and combinations of comparable agreement with experiment, but with \( v_1 \) being 53 cm\(^{-1} \) too low rather than too large and with \( v_2 \) being 114 cm\(^{-1} \) too low rather than being essentially correct (our error is only 4 cm\(^{-1} \); Table I). However, the vibrational levels they obtained variationally using an empirically adjusted multidimensional perturbed Morse oscillator surface are better than ours, with deviations from experiment of 5 cm\(^{-1} \) or less, or somewhat better than the agreement obtained earlier by Carter et al. \(^{6(a)} \) also using a variational method and an empirically adjusted potential energy surface. We conclude that our combined use of an \textit{ab initio} surface perturbation theory, and numerical integration to obtain the perturbed vibrational energies and wave functions is generally satisfactory for our semiquantitative needs as input to the UV band shape calculation, although not satisfactory for reproducing precise details of the ground-state IR spectrum.

The rotational constants \( B_x, B_y, B_z \) for the (000) level of both the \(^1A_1\) and \(^1B_2\) states are listed in Table III. Agreement\(^{33} \) is good.

Due to the many means of defining quartic centrifugal distortion constants, care should be exercised in comparing published values. This is because of different axis labeling

![Graph](image-url)

FIG. 4. Effect of anharmonicity upon ozone band origins. Energies are relative to potential minimum. Experimental energies from Ref. 5 except for the (020) state from Ref. 3(b).
schemes and because some prefer to report in the $r_{\text{adp}}$ themselves while others report in their experimentally determined linear combinations. In Table IV we adopt the latter usage, under the $I'$ representation and using the $\Delta_f$, etc. as defined in the appendix of Watson's paper. Direct comparison of this data to results obtained by the usual fitting procedure would be inappropriate and grossly underestimate the value of our calculations. A better set of $ab\ initio$ quartic centrifugal distortion constants for ozone has recently been obtained by us\cite{us34} at the HF/6-31G** and MCSCF levels using a new method\cite{tohnisaki} employing analytical $ab\ initio$ gradients.

A classical band shape calculation\cite{36,37} taking no account of vibrational structure is shown by Fig. 5. There is a temperature shift of the absorption maximum. This shift in frequency is positive with rising temperature, starting at 43220 cm$^{-1}$ at 0 K and at the three temperatures indicated represent a shift of 650, 1180, and 1980 cm$^{-1}$. In addition the bandwidth at half-height agrees with the trend that the classical bandwidth rises with temperature, and equals the quantum-mechanical bandwidth at $T = \infty$. (For a one-dimensional HO the ratio\cite{36} of classical to quantum bandwidths is $[\tanh x/x]^{1/2}$, where $x = hv/2kT$.) Note also the skewness of the spectra (third moment), a result of the non-identity of the ground- and excited-state vibrational frequencies.\cite{36}

Figures 6–10 illustrate several calculated spectra plus the experimental data.\cite{38} The energy scale has been red shifted 4620 cm$^{-1}$ for the synthesized spectra, and an arbitrary set of intensity units has been affixed to all diagrams. This ensures ease of comparison. All spectra shown were run for $T = 298$ K. The main features are shown by comparison of the experimental spectrum (Fig. 6) to the calculated spectrum for excitation from the (000) level alone (Fig. 7).

Not only has the proper overall band shape been realized, but also the effect of excitation into a vibrationally excited purely dissociative state is evident in the fine structure of the continuum. The numerical data reveals a series of progressions. There is a basic periodicity of some 820 cm$^{-1}$ and one of 340 cm$^{-1}$. As overlap of zeroth order HO functions is appreciable only for low values of vibrational quantum number, Fig. 8 suffices as a rough guide to the origin of the alternating 140 and 200 cm$^{-1}$ periodicity in the synthesized spectra. The region from $\nu_1$ to $2\nu_1$ is emphasized, although any other portion may have served by substitution of $(n + 1)\nu_1$ and $(n + 2)\nu_1$ for $\nu_1$ and $2\nu_1$, respectively. The experimental spectrum exhibits a similar structure, although the exact periodicity of the progressions awaits publication. Rotational broadening is seen in the smooth transition from one vibrational peak to the next. It is intriguing that such structure should be present in excitation to a dissociative state, illustrating the presence of diffuse vibrational structure in continuous UV spectra as treated by Pack.\cite{11} The Huggins system of bands is believed due to a $^1B_2 \leftrightarrow ^1A_1$ transition into a shallow well in the $^1B_2$ surface, allowing for sharpened vibrational structure.\cite{39} Our work is in agreement with this assignment, with a minimum at $r_2 = 3.585\ a_0, r_3 = 2.295\ a_0, \alpha = 74^\circ$ being located within the analytically fitted surface we employed.\cite{15,22} Note this is a $C_{2h}$ structure with an acute bond angle, in the excited state.

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**FIG. 6.** Experimental absorption spectrum from Ref. 38 at 300 K.

**FIG. 7.** Synthesized absorption from the (000) level with $T_{\text{exc}} = 298$ K. This spectrum as well as those in Figs. 9 and 10 have been red shifted by 4620 cm$^{-1}$.

**FIG. 8.** Explanation for progressions in synthesized UV spectrum.
When the calculation was performed at the theoretical 0 K for excitation out of the (000) level, only the $J = 0$ level is populated and one expects to see a diminution in the continuity of the progressions noted in Fig. 7. This is due to the absence of rotational broadening, and was "observed" for this computer "experiment" at absolute zero.

The suppression of rotational effects ($T_{rot} = 0$, $T_{vib} = 298$ K) diminished the quality of our calculated spectrum, as the rotational broadening disappears and we were unable to reproduce the experimental spectrum. Thus, it is likely that the effect of rotational broadening should be included if one seeks an improvement in the quality of calculated spectra. Comparison of Figs. 7 and 9 shows the agreement with experiment is good. From considering twenty rather than a single band. Again, the agreement with experiment is good.

Figure 10 shows the effect of including cross terms in the exited state vibrational wave functions, in effect the anharmonicity of the excited state. Comparison with Fig. 9 indicates that the effect of including anharmonicity is minor, at least for the excited state. Most likely this is a misrepresentation, as in both cases the $Q_1^+$ dissociative mode, the potential of which creates the overall band shape, was a harmonic barrier.

The key point is that explicit inclusion of higher order operators in the vibrational Hamiltonian did not markedly effect the calculated spectrum. Again we caution that the overall band shape did not account for anharmonicity in the $Q_1^+$ dissociative mode, so that future studies may prove this conclusion false.

**SUMMARY**

In conclusion we note what has been learned from this study. A new method is employed to generate electronic spectra based solely upon ab initio considerations. The method directly accounts for rotational broadening and vibrational anharmonicity. Upon application to ozone, a molecule of great theoretical and practical interest, the method shows that consideration of rotational broadening and quantized vibrational levels improves the fine structure of the absorption continuum, and lends support to the contention that vibrational fine structure is possible in a purely dissociative state. Vibrational anharmonicity has been shown to have a small effect, if any, upon the overall spectrum, although this may be a spurious result.

**ACKNOWLEDGMENTS**

The authors thank Dr. S. M. Blinder for his helpful suggestions and the University of Michigan Computing Center for use of its facilities.