Rovibronic Analysis of the Laser Induced Fluorescence Excitation Spectrum of the Jet-cooled Methoxy Radical

David E. Powers, Michael Pushkarsky and Terry A. Miller

Laser Spectroscopy Facility
Department of Chemistry
The Ohio State University
120 W. 18th Avenue
Columbus Ohio 43210

Abstract

The laser induced fluorescence excitation spectrum for the $\tilde{A}^2A_1 \leftrightarrow \tilde{X}^2E$ transition of the methoxy radical has been reinvestigated. An extensive set of vibrational levels has been assigned with the aid of increased vibrational and rotational cooling. Many of these vibrational assignments are confirmed by rotational analysis of bands involving both the symmetric and asymmetric fundamentals of the $\tilde{A}$ state as well as vibrations containing two quanta of the $e$ modes. Although parts of the vibrational structure have been assigned previously, several discrepancies are identified and corrected. Vibrational frequencies have been obtained for all the modes in the $\tilde{A}^2A_1$ state of the molecule. The Fermi resonance that exists between $\nu_3$ and $\nu_2$ has been investigated and interaction constants describing it have been obtained.

I. INTRODUCTION

The methoxy radical, CH$_3$O, is one of the most interesting organic radicals. In addition to the important role this molecule plays as a reaction intermediate in combustion and
atmospheric chemistry, it also holds a place of special significance for spectroscopists and theoreticians. With only 5 atoms and nominal $C_{3v}$ symmetry it is small enough to allow fairly sophisticated \textit{ab-initio} calculations\textsuperscript{1-7} of its electronic and geometric structure for the ground and lowest excited states. However, a number of factors, e.g., the interaction between the spin orbit splitting and the Jahn-Teller distortion in the ground state, curve crossings between low lying dibatic states, vibrational resonances, etc., complicate comparisons between experimental spectroscopic results and calculations.

Experimentally, the radical can be conveniently studied by a variety of optical techniques for which the strong oscillator strength of the transition from the ground state to the first excited state ($\tilde{A}^2A_1 \leftrightarrow \tilde{X}^2E$) lends itself well to laser induced fluorescence\textsuperscript{8-18} (LIF) and dispersed fluorescence (and emission)\textsuperscript{10,12,13,16,18-21} and more recently stimulated emission pumping (SEP) studies.\textsuperscript{22} Such experiments have led to considerable knowledge about the vibrational frequencies in the ground and excited electronic states. This strong electronic transition also makes the same techniques appealing for monitoring the reactions of methoxy but to be confident of the results it is necessary to have a good understanding of the electronic and vibrational levels involved.

Typically the LIF spectrum for a small molecule such as methoxy would be fairly unambiguous as one might expect to see allowed activity in the electronic spectrum for only the three totally symmetric vibrations in the molecule. In low resolution fast flow experiments\textsuperscript{13,16,17,21,23} this might appear to be true for methoxy but the amount of information from these type of experiments is limited due to overlap of the broad vibrational features. The flow system experiments were able to outline the general vibrational pattern for the excited state as involving a long progression of the C-O stretch. This is consistent with the lengthening of the C-O bond from 1.37 Å in the ground state to 1.58 Å in the first excited state\textsuperscript{11} due to a promotion of an electron from the C-O bond to a non-bonding orbital mostly localized on oxygen.

Cooling allows one to obtain more information on the vibrational frequencies of the molecule. Various jet expansion studies\textsuperscript{9-12,14,15,18,20} have been performed over the past 15
years and a number of the vibrational frequencies have been determined for the $\tilde{A}$ excited state but there have also been some problems associated with these studies. For a considerable time, even the frequency of the origin of the electronic transition was under dispute with a variety of values reported in the literature (for more information see Foster et al.\textsuperscript{12}). Various papers have reported a few of the vibrational frequencies but a complete picture is only now coming into view. There are a number of reasons for the difficulties in obtaining a good vibrational assignment for the $\tilde{A}$ state vibronic levels observed in the LIF excitation spectrum of methoxy, not the least of which is the large rotational constants. Even very cold rotational spectra of individual vibrational bands of methoxy can span as much as 40 cm$^{-1}$ and overlap of these rotational features are common. The overlap of the vibrational bands would be less of a problem if not for the activity of the normally forbidden $e$ vibrations in the excited state, which are allowed at least in part by the $^2E$ symmetry of the $\tilde{X}$ state and presence of the Jahn-Teller distortion. This greatly increases the number of transitions in the LIF spectrum and further intensifies the overlap of vibrational levels.

Another complication in the vibronic analysis is the Fermi resonance which first occurs between $\nu_3$ and $2\nu_2$ and continues throughout the spectrum. The Fermi resonance yields a multiplet of features each separated by roughly 30 to 50 cm$^{-1}$ (about the width of the rotational structure for an individual band) adding to the congestion. A final complicating factor is the presence of hot bands. Even under conditions which would normally yield vibrationally cold LIF spectra, methoxy still shows a multitude of strong hot features. These hot features greatly complicate the spectrum making the low frequency region, where one would expect only a few vibrational features, very congested. The combination of these factors has led to past misassignments that we will address in this paper.

It might appear that a few incorrect assignments of the excited state vibrations would not be too important in the long run. However it is imperative to have accurate assignments for methoxy in order to benchmark theoretical calculations and to perform other experiments on the molecule. There has for some time been a great deal of spectroscopic interest in
the ground state of methoxy. The degenerate ground state which is subject to the Jahn-
Teller distortion and its interaction with the spin-orbit coupling is an interesting and very
complicated situation which is still not fully understood. Dispersed fluorescence and SEP
studies can be used to get a handle on the vibrational structure in the ground state but it
is necessary to know the vibrations in the excited $\tilde{A}$ state used in these studies, to interpret
the $\tilde{X}$ state structure. In a later paper\textsuperscript{24} we will present photofragmentation studies on
methoxy that reveal quite mode and frequency dependent photochemistry. The analysis of
these results would be impossible without the excited state assignments presented herein.

To this end we have reexamined the LIF spectrum of methoxy using several tools which
have not been consistently available in past studies. These tools include good vibrational
and rotational cooling (absence of all hot vibrational features) and rotational analysis of
most of the bands observed. With a combination of these aids we have been able to obtain
a much more complete assignment of the vibronic structure of the LIF spectrum and obtain
good vibrational frequencies for the $\tilde{A}$ state of CH$_3$O.

During the course of this work, we became aware of similar studies being carried out in
the laboratory of F. Temps. We have compared our results and where they overlap have
found consistency. A complete account of the work of Temps and co-workers can be found
elsewhere.\textsuperscript{25,26}

II. EXPERIMENTAL

The free jet expansion and most experimental considerations for this study have been
presented previously\textsuperscript{12} but will be briefly summarized here. The methoxy radicals were
formed by photolysis of methyl nitrite seeded in helium carrier gas by a KrF excimer laser
(Lumonics Excimer-500). The expansion was formed using a commercial pulsed nozzle
(Newport BV-100) with a 0.75-mm orifice. In order to achieve maximum vibrational cooling
of the molecules and to eliminate hot bands from the LIF spectrum a teflon fixture as
described by Powers et al.\textsuperscript{15} was attached to the nozzle. This fixture consisted of a teflon disk
0.5 cm thick with a pre-expansion channel 2 mm. in diameter. The photolysis laser crossed the pre-expansion channel in the center of the teflon disk thereby allowing the hot radicals to partially cool prior to the final expansion. The backing pressure of helium used when the teflon fixture was attached was about 20 atm. Although the vibrational temperature was much lower when the fixture was used, the rotational temperature was slightly higher (typically about 5 K with the fixture and 2 K without), but still lower than in our previous study.\textsuperscript{11}

The probe laser, which crossed the expansion about 2.5 cm downstream was a frequency doubled XeCl (308 nm) excimer-pumped dye laser (Lambda Physics EMG-103-MSG pumping a Lumonics HyperDye-300 dye laser). The fluorescence from the methoxy radicals was collected with an f1 quartz lens and projected onto an EMI 9659QB photomultiplier tube. The signal from the multiplier was sent to a transient digitizer (LeCroy 2262) and then stored on computer. All laser frequency calibration was performed using a Burleigh WA-4500 wavemeter. The error limits in the frequency assignments is a combination of the wavemeter accuracy, the laser linewidth and scanning jitter of the dye laser. The dye laser jitter is manifest periodically as a jump of \( \leq 0.5 \text{ cm}^{-1} \). In an effort to reconcile this jitter, multiple scans were utilized. From calibration of multiple scans the estimated absolute accuracy of our values is \( \pm 0.5 \text{ cm}^{-1} \).

The synthesis of the methyl nitrite, as described previously\textsuperscript{12}, was made by dropwise addition of dilute sulfuric acid to a solution of sodium nitrite and methyl alcohol. The gaseous product was collected and used from a reservoir held at the temperature of a dry ice isopropyl alcohol bath.

\textbf{III. VIBRATIONAL ASSIGNMENTS OF THE \( \tilde{\text{A}} \ ^{2}\text{A}_{1} \) STATE}

The LIF spectra reported here were taken using the teflon fixture discussed in the experimental section. Without the fixture the spectra were complicated by many vibrational hot bands of methoxy. Fig. 1 shows a comparison of a small region of the methoxy LIF
spectrum with and without the fixture. Methoxy appears to be unusual in the number and intensity of hot vibrational features observed for a jet-cooled molecule. The assignment of these hot bands is complicated by a relatively poor understanding of the ground state vibrational frequencies. The large rotational constants for the molecule causes many of the rotational lines due to hot and cold features to overlap. This overlap greatly complicates the assignment of the transitions and makes it very difficult to use the rotational structure to aid in the assignment of the band. After placing the fixture on the nozzle we typically observed no vibrational hot bands. In cases of doubt, we were able to verify that the observed features were not hot bands using the fluorescence depletion technique. This approach immediately resolved some of the remaining assignment questions and aided in identifying some new, weak cold features (such as the transitions involving two quanta of $e$ symmetry modes).

Our experimental observations are summarized in Table I. A few words of explanation are in order concerning frequencies reported in this table. The table represents the energy difference between the origin of the vibrationless level of the $\tilde{A}^2A_1$ state (obtained from the rotational analysis described in Section IV) and the origin of the given vibronic level. The absolute frequency of the electronic origin, $\nu_{00}$, (as defined previously) is determined independently in the present experiments to be $31614.1 \pm 0.5 \text{ cm}^{-1}$. There has in the past been significant controversy concerning the position of the electronic origin. A summary of the previous values can be found in Foster et al. and will not be reiterated here. Within the somewhat larger error limits of the current experiment (due mainly to fewer rotational lines in the colder spectra), the value of the present origin agrees well with previous work ($31614.51(4) \text{ cm}^{-1}$) from this lab although the calibration procedures were entirely different.

Since the actual spectrum arises from transitions out of the $^2E_{3/2}$ level which is off-set from the origin of the $\overline{X}$ state by approximately half the spin-orbit coupling, it is convenient to indicate an effective origin near the center of the bands. Thus we choose to add the energy, $30.11 \text{ cm}^{-1}$, of the $^2E$ origin above the lowest ($K = 0$, $J = 1/2$) level of the $^2E_{3/2}$ state. Therefore we take the absolute frequency of the effective origin of the $0^0_0$
transition as 31644.2 cm\(^{-1}\). Ergo, it follows, for example, that the arrow indicating the effective origin of the 3\(^2\) transition in Fig. 2 (and later comparable figures) is located at 31644.2+1319.3=32963.5 cm\(^{-1}\).

Fig. 3 displays the vibrational modes of methoxy. The atomic displacements are based upon \textit{ab initio} calculations\(^{28}\) for the \(\tilde{A}\) state using ROHF/6-31G*. There are 3 non-degenerate totally symmetric \((a_1)\) modes which as Fig. 3 shows can be roughly described as the symmetric C-H stretch \((\nu_1)\), the CH\(_3\) umbrella motion \((\nu_2)\), and the CO stretch \((\nu_3)\). The other 3 modes are doubly degenerate and of \(e\) symmetry. Again following Fig. 3, these are qualitatively described as the asymmetric C-H stretch \((\nu_4)\), the C-H scissors bend \((\nu_5)\), and the methyl rock \((\nu_6)\). Using the improved cooling achieved with the use of the teflon fixture in conjunction with rotational resolution and frequency information, vibrational assignments of most of the features in the LIF spectra were achieved unambiguously. With the elimination of the congestion due to hot features, the fundamentals of the lower frequency modes can readily be identified and assigned. Assignment of the progressions and combinations is aided by the uniqueness of the rotational signatures for any bands containing respectively, zero, one, or two quanta of a particular \(e\) mode as described later. Typically the appearance of a Fermi resonance in a spectrum can be a complicating feature but for methoxy it can actually be used effectively to aid in the assignment. As is described in Section III C, the \(\nu_2, \nu_3\) interaction can be observed through the entire progression and in fact in combinations with all the other observed modes. The interaction gives rise to a characteristic multiplet pattern which can be used to help in assigning individual quantum numbers. A combination of these features and techniques has led to the following \(\tilde{A} \ ^2\text{A}_1\) vibrational assignments.

A. Symmetric modes

\textit{Ab-initio} calculations predict\(^1\), and the rotational analysis\(^{11}\) has verified, a large lengthening of the C-O bond length in the excited state relative to the ground state in methoxy.
This lengthening of the bond yields a long progression of the C-O stretch ($\nu_3$) of about 660 cm$^{-1}$ which dominates the methoxy LIF spectrum. The lowest vibrational feature observed in the LIF spectrum (662.4 cm$^{-1}$) has been assigned to $\nu_3$. The assignment of this band as the fundamental of the CO stretch is consistent with \textit{ab-initio} calculations\textsuperscript{7}. There appears to be general agreement in this assignment with previous work.

As a general rule, the $\nu_3$ progressions involve multiple components due to a Fermi resonance caused by a near coincidence between the frequency of $\nu_2$ and two quanta of $\nu_3$. For example, the first overtone of $\nu_3$ exists in a Fermi resonance with $\nu_2$ the fundamental forming the doublet structure observed at 1289 and 1319 cm$^{-1}$ above the origin (see Table I). Although this structure has been seen in many of the other studies on methoxy\textsuperscript{12,14,15,20} there is some disagreement in the literature as to which of these components can be better described as $\nu_2$ and which as $\nu_3$. Foster et al.\textsuperscript{12} indicate that the lower frequency component is predominantly $3^2$ and the upper $2^1$ based on dispersed fluorescence data. Brossard et al.\textsuperscript{20} assign these features in the other order. Misra et al.\textsuperscript{10} agree with Foster presumably based on their dispersed work. In some more recent work, Lee et al.\textsuperscript{18} utilize dispersed fluorescence Franck Condon Factors to argue that the lower frequency component contains more $\nu_2$ character and is best fit by mixing the $\nu_2$ and $2\nu_3$ wavefunctions with a ratio of 1.43:1. This argument is also consistent with the comparison between CH$_3$O and CD$_3$O vibrational frequencies\textsuperscript{12} for which deuterating the molecule caused only a small change in the frequency of $3^1$ (660 cm$^{-1}$ for CH$_3$O and 663 cm$^{-1}$ for CD$_3$O) as well as only a small change in the higher frequency component (1315 cm$^{-1}$ for CH$_3$O and 1319 cm$^{-1}$ for CD$_3$O) but a much larger change (1287 cm$^{-1}$ for CH$_3$O vs 971 cm$^{-1}$ for CD$_3$O) for the other band. Upon deuteration, one would expect a smaller change for the CO stretch than for the umbrella mode. We have investigated this situation using the Fermi calculations presented in Section III C. Our results indicate that the wavefunction for the lower energy vibrational state of the Fermi doublet is predominately $2^1$ and the upper level contains more $3^2$ as can be seen by looking at the corresponding wavefunctions (see Table II).

The near coincidence between the frequencies for combinations involving $x$ quanta of
$\nu_3$ and $y$ quanta $\nu_2$ continues up to $m = 6$ (where $m = x + 2y$) in the LIF spectra. An additional three members of the progression have been observed using the fluorescence depletion technique$^{24}$ and have been included in our analysis in Section III C. Where we do not wish to distinguish between the components of the multiplets we shall use the notation, $(\nu_2 + \nu_3)^m$, to denote a given member of the progression.

The third symmetric mode $\nu_1$ (the symmetric C-H stretch) has been assigned to a weak feature at 2947.8 cm$^{-1}$. This feature has not previously been reported presumable because it lies on the wing of fairly strong vibrational band. The assignment of this feature as $1^1$ has been made for a number of reasons. This band has the correct rotational profile to be a symmetric mode and there are no other possible symmetric combinations unaccounted for in this region. In addition, this frequency is consistent with the ab-initio calculations of Morokumo$^7$ and our own.$^{28}$ There is also good agreement between this value and that obtained for similar molecules$^{29}$ (CH$_3$F at 2965 cm$^{-1}$, and CH$_3$Cl at 2966 cm$^{-1}$). A band previously$^{12}$ identified as $\nu_1$ has been reassigned to $3_{0}^{1}5_{0}^{1}6_{0}^{1}$ (see Table I), based upon its rotational structure. Two combinations of $\nu_1$ with the multiplet $(\nu_2 + \nu_2)^3$ have been observed at 4705.9 and 4743.6 cm$^{-1}$. The other combinations of the $\nu_1$ band with $(\nu_3 + \nu_2)^3$ were not observed but their calculated positions lie under other strong features in the spectrum.

The assignments of all the symmetric bands are summarized in Table I. The molecular constants describing these modes are summarized in Table III.

### B. Asymmetric Modes

The band at 929.5 cm$^{-1}$ has been assigned to the lowest frequency $e$ vibrational mode $\nu_6$ (rocking motion). Nominally this band, along with the other $e$ modes, is observed because the vibrationless level of the $\tilde{X}$ state contains some $e$ character due to the Jahn-Teller effect. Previously the frequency of $\nu_6$ was reported$^{12}$ at 595 cm$^{-1}$. This latter band is due to a hot band which was observed in this work when the expansion fixture was not used but which was completely cooled out in spectra taken with the fixture. The assignment of $\nu_6$ at 929.5
cm$^{-1}$ is in line with other similar molecules\textsuperscript{29} (CH$_3$F at 1196 cm$^{-1}$, CH$_3$Cl at 1015 cm$^{-1}$).

The rotational structure of $\nu_6$ is very distinct and is discussed in Section IVB2. This structure was used to help identify combination bands involving $\nu_6$. A progression of $\nu_6$ with the $(\nu_3 + \nu_2)^m$ multiplets has been observed up through $m = 6$ although a few of the components of some of the multiplets are not observed due to low intensity. All these features have the same distinctive rotational profiles and can unambiguously be identified by this characteristic.

Our assignment of the fundamental of $\nu_5$ at 1403 cm$^{-1}$ is in agreement with previous works.\textsuperscript{12} The assignment of this frequency to the scissors motion is very much in line with similar molecules\textsuperscript{29} (CH$_3$F at 1471 cm$^{-1}$ and CH$_3$Cl at 1455 cm$^{-1}$). Once again this vibration has a very distinctive rotational signature which can be used in the assignment (see Section IVB2). The mode $\nu_5$ is seen to exist in a long progression of combinations with the $(\nu_3 + \nu_2)^m$ Fermi multiplets. These features again have the distinctive rotational signatures of $\nu_5$ and can easily be identified by this structure.

The fundamental of the asymmetric C-H stretch ($\nu_4$) has not been observed in this work but combinations of this band with $\nu_3$ have. The rotational structure of $3^1_04^1_0$ band (3740.2 cm$^{-1}$) has the general characteristics of all vibrations containing $e$ mode in CH$_3$O. There is a significant Coriolis coupling which widens the band (discussed in Section IVB2). Although the general appearance of this feature is similar to that of $\nu_6$ it is different enough to be easily distinguished. Previous work had assigned this band as $1^1_03^1_0$ but it does not have the correct rotational structure to be a totally symmetric vibration. This feature is not assigned as the fundamental because the frequency of 3740.2 cm$^{-1}$ is too high (by about the frequency of $\nu_3$) when compared with \textit{ab-initio} calculations\textsuperscript{7,28} and with similar molecules\textsuperscript{29}. There is a band about 655 cm$^{-1}$ lower in energy which could be the fundamental but this band does not have the same rotational signature as the 3740.2 cm$^{-1}$ band and we therefore do not assign this feature to the fundamental of $\nu_4$ (this feature is discussed further below). Assigning the 3740.2 cm$^{-1}$ band as $3^14^1$ would give a $\nu_4$ frequency of about 3072 cm$^{-1}$ which is in line with the calculations and with similar molecules. Additional combinations of $\nu_4$
with the \((2^1 + 3^2)\) Fermi doublet have also been observed (see Table I).

There are a number of features in the LIF spectrum which have been assigned to vibrations involving two quanta of \(\nu_6\), two quanta of \(\nu_5\) or one quanta each of \(\nu_6\) and \(\nu_5\). For these modes, \(l = 0\) and \(\pm 2\) giving rise to an \(a\) and an \(e\) symmetry vibrational level. The rotational structure of these features will be discussed in Section IV B 2. The features at 1843 cm\(^{-1}\) (\(a\) symmetry) and 1846.6 cm\(^{-1}\) (\(e\) symmetry) constitute the first overtone of \(\nu_6\). Also seen is the combination of \(2\nu_6\) with \(3^1\) at 2464.2 cm\(^{-1}\) (\(a\) symmetry) and 2468.2 cm\(^{-1}\) (\(e\) symmetry). The next 3 members of the progression, \((\nu_2 + \nu_3)^m\) in combination with \(2\nu_6\) have also been observed. For the last two of these features only one component of the Fermi resonance multiplet is seen.

In a similar way, both \(a\) and \(e\) bands are observed corresponding to \(2\nu_5\) near 4100 cm\(^{-1}\). Combinations of \(2\nu_5\) with \(2^13^1\) and \(3^3\) are observed near 4720 and 4756 cm\(^{-1}\), respectively.

Another long series of features involving 2 quanta of \(e\) symmetry are combinations with one quanta each of \(\nu_6\) and \(\nu_5\). The lowest frequency component of this sequence is at 2321.3 cm\(^{-1}\) (\(a\) symmetry) and 2323.8 cm\(^{-1}\) (\(e\) symmetry) with combinations with \((\nu_2 + \nu_3)^m\) near 2965, 3600, 4205, 4815 cm\(^{-1}\).

The \(e\) vibrational band assignments are also contained in Table I. As with the \(a\) modes, the resulting vibrational parameters for the \(e\) modes are given in Table III.

### C. Fermi resonance

In the methoxy radical the frequencies of all combination levels of \(x\nu_2\) and \(y\nu_3\), \((\nu_2 + \nu_3)^m\), where \(2x + y = m\), \(x = 0, 1, 2, \leq m/2\ldots, m = 2, 3\ldots\) are nearly degenerate. In this case anharmonic terms of the potential may cause significant perturbation, and such cases are referred to as Fermi resonances. To obtain the vibronic energy levels in such a case diagonalization of the Hamiltonian matrix should be employed. The Hamiltonian, \(\mathcal{H}_F\), for a Fermi resonance interaction of two symmetric modes may be written as

\[
\mathcal{H}_F = \mathcal{H}_{OSC} + \mathcal{H}_3 + \mathcal{H}_4
\]

(1)
where $\mathcal{H}_{\text{OSC}}$ is the harmonic oscillator Hamiltonian for the two modes, $\nu_2$ and $\nu_3$, and $\mathcal{H}_3 + \mathcal{H}_4$ denote the anharmonic terms which we take to be truncated at the third and the fourth powers of the expansion of the potential energy in the $Q_2$ and $Q_3$ normal coordinates.

The eigenfunctions of $\mathcal{H}_{\text{OSC}}$ are well known

$$\mathcal{H}_{\text{OSC}} | \nu_2, \nu_3 \rangle = \hbar [\omega_{\nu_2} \cdot (v_2 + 1/2) + \omega_{\nu_3} \cdot (v_3 + 1/2)] | \nu_2, \nu_3 \rangle$$

where $v_2, v_3$ and $\omega_2, \omega_3$ are respectively the number of quanta and the harmonic vibrational frequencies of the $\nu_2$ and $\nu_3$ modes respectively. $\mathcal{H}_3$ and $\mathcal{H}_4$ may be written as:

$$\mathcal{H}_3 = a_1 Q_2^3 + a_2 Q_2^2 Q_3 + a_3 Q_2 Q_3^2 + a_4 Q_3^3$$

and

$$\mathcal{H}_4 = \alpha_1 Q_2^4 + \alpha_2 Q_2^3 Q_3 + \alpha_3 Q_2^2 Q_3^2 + \alpha_4 Q_2 Q_3^3 + \alpha_5 Q_3^4$$

where $a_i$ and $\alpha_i$ are coefficients of expansion.

The eigenstates of $\mathcal{H}_{\text{OSC}}$ will serve as basis for construction of the matrix of $\mathcal{H}_F$. In principle, $\mathcal{H}_F$ connects all the basis functions. However, for our purposes it has proved sufficient to truncate the $\mathcal{H}_F$ matrix to the subspace of the levels defined by each multiplet $(\nu_2 + \nu_3)^m$. We consider only the values of $\mathcal{H}_4$ diagonal in that subspace. Using a Van Vleck transformation $\mathcal{H}_3$ within the space can be represented by an effective operator

$$\mathcal{H}_3' = q_F(a_2 a_3^+ a_3^+ + a_2^+ a_3 a_3)$$

where $a^+$ and $a$ are creation and destruction operators for the harmonic oscillator.

Nonzero matrix elements for $\mathcal{H}_F$ within the subspace are explicitly:

$$\langle \nu_2, \nu_3 | \mathcal{H}_F | \nu_2, \nu_3 \rangle = \omega_{\nu_2} (v_2 + 1/2) + \omega_{\nu_3} (v_3 + 1/2) - \omega_{\nu_2} x_{\nu_2} (v_2 + 1/2)^2$$

$$- \omega_{\nu_3} x_{\nu_3} (v_3 + 1/2)^2 - \omega_{\nu_2} x_{\nu_2} x_{\nu_3} (v_2 + 1/2) (v_3 + 1/2)$$

$$\langle \nu_2 + 1, \nu_3 - 2 | \mathcal{H}_F | \nu_2, \nu_3 \rangle = q_F \sqrt{(v_2 + 1)(v_3 - 1)v_3}$$
along with their Hamiltonian counterparts.

A least-squares fit of the eigenvalues of $H_F$ were made to the experimentally measured energies of the multiplet levels, with the variables, $\omega_{e2}$, $\omega_e x_{e2}$, $\omega_{e3}$, $\omega_e x_{e3}$, $\omega_e x_{e23}$, and $q_F$. The fit values of the variables are given in Table III. The eigenvalues and eigenfunctions obtained with the fit variables are given in Table II, where the former are compared with the observed energies. In general, the comparison between the calculated and observed energies is very good. The standard deviation of the fit for 18 lines is 1 cm$^{-1}$, comparable to the experimental measurement error, with a maximum deviation of 2.4 cm$^{-1}$.

The eigenfunctions obtained from the fit demonstrate that the vibrational levels are no longer pure harmonic oscillator functions but rather their linear combinations. Moreover in most of the analyzed 18 vibrational levels at least two basis vectors have comparable weights which indicates that vibrational modes are strongly mixed. When eigenfunctions are combinations of basis set vectors with comparable weights it is difficult to provide consistent nomenclature to identify the levels. In this paper (see particularly Table I) we will use the following approach to conveniently label the individual levels within a $(2\nu_2 + \nu_3)^m$ multiplet.

Typically one would label a given eigenstate by the basis vector with the largest absolute value of its coefficient and we follow this convention. However for methoxy, in several cases within one Fermi resonance multiplet more than one eigenfunction may have as its largest contributor the same basis vector. In this case the state having the largest absolute value of coefficient for this basis vector maintains the label of that basis vector. The other state is labeled by the largest basis vector of the remaining set.

For example, consider the multiplet with $m=5$ whose calculated energies and eigenvectors, as well as vibrational assignments, are shown in the Table II. The fourth column contains the energies of computed vibrational levels, the fifth through eighth columns show coefficients for the basis vectors $3^5$, $2^13^3$ and $2^23^1$ which constitute the vibrational Fermi resonance eigenstates and column 2 shows the assignment made using the algorithm described above. The calculated level at 3218.1 cm$^{-1}$ contains the $2^23^1$ basis vector with the largest weight, 0.78, and is labeled $2^23^1$. The levels calculated at 3183.0 cm$^{-1}$ and 3261.8 cm$^{-1}$
both have the $2^13^3$ basis vector present with the largest weight, with coefficients -0.68 and 0.73 respectively. According to the algorithm the level at $3261.8 \text{ cm}^{-1}$ has the larger weight and is assigned the label $2^13^3$ while the remaining level at $3183.0 \text{ cm}^{-1}$ gets the label of the last available basis vector, $3^5$. It should be emphasized that such labels do not represent the actual structure of the vibrational levels. In order to fully understand the structure of the Fermi mixed levels one must consult Table II for the complete eigenvalue and eigenfunction information.

Table I, containing the assignment of all the observed bands in the LIF spectrum, is labelled using this algorithm. In cases when the vibrational state is a combination of an $e$ symmetry mode with a member of the Fermi resonance multiplet it has been assumed that the structure of the multiplet is not affected by excitation of additional $e$ mode.

D. Perturbed Bands

About 10 percent of the bands for which we have obtained rotationally resolved spectra are entered into Table I without a vibrational assignment. The reason for this is that the structure of these bands did not match that expected for bands terminating in vibronic levels of the types previously considered. Generally speaking there could be a couple of reasons for the unusual structure of these bands. They might belong to overtones or combinations involving excitation of three or more quanta of $e$ vibration. However given the weakness of the bands involving only two quanta, it seems unlikely that all, or even most, of the remaining bands can be so explained. Rather we suspect many, perhaps all, of the remaining lines have rotational structure differing from the usual patterns because of Coriolis perturbations between different vibronic levels. If strong enough, such perturbations could give rise to virtually unique structure for each level, the analysis of which being a nearly impossible task based upon the present data.

In the absence of assignable rotational structure, one must rely on the band frequencies alone for assignments. However, these assignments are clearly speculative particularly
because all the bands are high enough in frequency so that multiple possibilities exist for most. However, it seems reasonable to suggest our most likely candidates for several of the unassigned bands in Table I. The feature at 3854 cm$^{-1}$ could be assigned as either 1$^{1}6^{1}$ or 3$^{1}5^{1}6^{2}$. Either is a likely prospect on the basis of frequency but one would expect the 1$^{1}6^{1}$ feature to rotationally resemble other combinations of symmetric modes with $\nu_{6}$ which it does not. On the other hand, one expects little intensity for the 3$^{1}5^{1}6^{2}$ band. If one adds approximately the frequency of one quanta of $\nu_{3}$ to this band there are two features in the Table I in that region, at 4463 and 4518 cm$^{-1}$. Either of these features could be 1$^{1}3^{1}6^{1}$. On the other hand the two features could be assigned as the Fermi doublet for 3$^{2}5^{1}6^{2}$ and 2$^{1}5^{1}6^{2}$. The feature at 5126 cm$^{-1}$ can then be the next member of that progression with another quanta of $\nu_{3}$.

If one starts with the 4359 cm$^{-1}$ band a similar argument may be presented. This feature could be either 1$^{1}5^{1}$ or 3$^{1}5^{2}6^{1}$ but again a satisfactory rotational fit has not been achieved. There is still a third possibility for this feature as the second Fermi component of the 2$^{1}4^{1}$ and 3$^{2}4^{1}$ multiplet which has not been located but here again the rotational structure is not adequately fit. The feature at 5057 cm$^{-1}$ is likely assigned as a combination of the 4359 cm$^{-1}$ band with $\nu_{3}$.

IV. ROTATIONAL ANALYSIS

A. Theory

In this work, we have made extensive use of the rotational analysis of transitions from the vibrationless level of the $\bar{X} \; ^{2}E$ electronic state (of overall $e$ vibronic symmetry) to different types of vibronic levels of the $\bar{A} \; ^{2}A_{1}$ excited electronic state of the methoxy radical. Transitions to symmetric levels ($0^{0}$ and $3^{1}$) of the $\bar{A}$ state have been analyzed previously$^{11}$ while those to $e$ symmetry vibrational levels have attracted much less attention in part because of the lack of experimental spectra. To make the description of the rotational
analysis complete and uniform we begin with a brief overview of the theory of the rotational structure of both the a and e symmetry vibronic levels and the intensities of the LIF spectra of transitions between those levels.

1. Doublet Vibronic Levels of e Symmetry

Having in mind using a Hund’s case a basis set we can define the angular momentum vectors in the system as follows:

\[ \mathbf{J} = \mathbf{S} + \mathbf{N} \]  

and

\[ \mathbf{N} = \mathbf{L} + \mathbf{G} + \mathbf{R} \]

where

- \( \mathbf{J} \) = total angular momentum of the molecule
- \( \mathbf{S} \) = electronic spin
- \( \mathbf{L} \) = electron angular momentum
- \( \mathbf{G} \) = vibrational angular momentum
- \( \mathbf{R} \) = angular momentum associated with rotation of a molecule as a whole

Following Hougen’s notation\(^{30}\) we specify the two components of the e symmetry vibronic function as \(|e_{\pm}\rangle\) where the subscripts + and - are determined by the transformation properties of the vibronic functions as follows:

\[ C_3 | e_{\pm}\rangle = e^{\pm 2\pi i/3} | e_{\pm}\rangle \]  

\[ \sigma_{xz} | e_{\pm}\rangle = | e_{\pm}\rangle \]

where the symmetry operators have their usual significance in \( C_{3v} \) symmetry.

The overall vibronic basis function \(|e_{\pm}\rangle\) can be initially represented as \(|i\rangle|v\rangle\) where the electronic wavefunction \(|i\rangle\) is denoted \(|E\rangle\) for the \( \bar{X} \) \( ^2\)E state and \(|A\rangle\) for the \( \bar{A} \) \( ^2\)A\(_1\) state.
and $|v\rangle$ is a vibrational function. In the case of the $\tilde{X}$ $^2$E electronic state with possible Jahn-Teller distortion the vibronic functions $|e_{\pm}\rangle$ may be assumed to be a linear combination of the simple products functions, as such states cannot be rigorously separated into a vibrational and electronic part. However, in the case of the $^2$A, electronic state we do not expect to have strong vibronic coupling and for most purposes the simple products should suffice.

Upon adding rotational and electronic spin factors we obtain a “Hund’s case a” basis set, $|e_{\pm}, J, P, S, \Sigma\rangle$ for a given $e$ vibronic state:

$$| e_{\pm}, J, P, S, \Sigma\rangle = | e_{\pm}\rangle | J, P, M\rangle | S, \Sigma\rangle$$

(12)

where the ket $| J, P, M\rangle$ corresponds to rotational wavefunction with $P$ and $M$ being respectively the projection of $J$ on the molecular and space fixed z axes and an electronic spin ket $| S, \Sigma\rangle$ with projection ($\Sigma$) on the molecule fixed symmetry axis. It has been found convenient to use symmetric and antisymmetric combinations of functions (Eq. 12) with opposite signs of the molecular fixed projections:

$$| J, P, S, \Sigma, \pm\rangle = \frac{1}{\sqrt{2}}\{ | e_{+}\rangle | J, P, M\rangle | S, \Sigma\rangle \pm (-1)^{J-P+S-\Sigma} | e_{-}\rangle | J, -P, M\rangle | S, -\Sigma\rangle\}$$

(13)

These functions are eigenfunctions of the xz reflection of the $C_{3v}$ symmetry group for the total molecule (acting on all coordinates) as described by Hougen$^{30}$:

$$\sigma_{xz} | J, P, S, \Sigma, \pm\rangle = \pm | J, P, S, \Sigma, \pm\rangle$$

(14)

The quantum number associated with this reflection is called parity with values, $\pm 1$.

*a. $^2$E Hamiltonian:* In the present paper we accept the effective rotational Hamiltonian for the $^2$E state used by Liu, et al.$^{11}$ to describe the rotational structure of the $e$ vibronic levels of either the $\tilde{A}$ or $\tilde{X}$ state. The total Hamiltonian, $\mathcal{H}_{TR}$, consists of a number of terms which can be classified as a rotational Hamiltonian, $\mathcal{H}_R$, spin-orbit, $\mathcal{H}_{SO}$, and spin-rotation interactions, $\mathcal{H}_{SR}$, as well as a number of terms which are responsible for centrifugal distortion and higher order contributions to the first terms, $\mathcal{H}_{CD}$,
\[ H_{TR} = H_{ROT} + H_{COR} + H_{JT} + H_{SO} + H_{SR} + H_{CD} \]  

(15)

In writing Eq. (15) we have decomposed \( H_R \) into a Coriolis term, \( H_{COR} \) and a Jahn-Teller term, \( H_{JT} \), with the remainder of \( H_R \) residing in \( H_{ROT} \). It is important to note that while \( H_{TR} \) was used previously exclusively for the vibrationless level of the \( \tilde{X} \) \( ^2E \) state, its form is appropriate for any \( ^2e \) vibronic level. Obviously the magnitude of the parameters will be strongly dependent upon the state to which it is applied.

As it has been mentioned earlier, in the present work we deal with a small number of lines for our relatively rotationally cold spectra (\( \leq 7K \)) and with an experimental resolution of 0.2 cm\(^{-1}\). Under these conditions we could not detect the effects of \( H_{JT} \) and \( H_{CD} \). Hence we will omit these terms for the remainder of this paper. However if the resolution or rotational temperature of the spectrum increases these terms will become important and should be included.

The remaining four terms of \( H_{TR} \) are written explicitly:

\[ H_{ROT} = A(J_z - S_z)^2 + B(J^2 - J_z^2) - 2B[J_x S_x + J_y S_y] \]  

(16)

\[ H_{COR} = -2A\xi_t N_z \]  

(17)

\[ H_{SO} = aL_z S_z \]  

(18)

\[ H_{SR} = e_{aa} N_z S_z + \frac{1}{2} e_{bc}(N_+ S_- + N_- S_+) \]  

(19)

\( A \) and \( B \) are the standard symmetric top rotational constants and \( a, e_{aa} \) and \( e_{bc} \) are respectively the effective spin orbit and spin rotational interaction constants with \( \xi_t \) the component of vibronic angular momentum along the symmetry axis. All these constants have been explicitly defined previously.\(^{11}\) To be consistent with previously published matrix elements\(^{31}\) and usage\(^{11}\), a term, \(-\frac{1}{2}B\), is added to the zero of energy.
b. Doublet Vibronic Levels of $a_1$ Symmetry  

For $^2a_1$ (or $^2a_2$) vibronic states, a general symmetrized case b basis function is more appropriate and can be written

$$\left| a, J = N \pm 1/2, K, M_j, N, S, \pm \right> = \sum_{M_SM_S} (-1)^{N-S+M_j}(2J+1)^{1/2}$$

with $| a \rangle$ a vibronic function of $a$ symmetry and

$$| N, K, M_N, \pm \rangle = 2^{-1/2}(|N, K, M_N \pm (-1)^{N-K}|N, -K, M_N\rangle)$$

where $K$ and $M_N$ are respectively the projections of $N$ along the molecule's 3-fold axis and the space-fixed axis. For $K=0$ the simple ket $|N,0, M_N\rangle$ obviously suffices.

As long as we deal with $a_1$ symmetry vibronic states of the $^2A_1$ electronic state the expectation values of electronic and vibrational angular momentum vanish. In addition no spin rotation splitting and centrifugal distortion effects were experimentally resolved. Thus one can reduce $\mathcal{H}_{TR}$ to

$$\mathcal{H} = B N^2 + (A - B) N_z^2$$

This $\mathcal{H}_{RT}$ may be evaluated in the case (b) basis above, yielding only diagonal values, leading to the standard expressions for symmetric top rotational energies.

2. Transition intensities.

In order to complete the consideration of the rotational structure one needs to provide expressions for intensities of transitions between rovibronic levels. In the LIF process, molecules absorb laser photons with frequency, $\nu_i$, and polarization, $\mu_i$, and are excited from initial level $A$ to an excited level $B$, followed by emission of photons of frequency, $\nu_f$, and polarization, $\mu_f$, to a final state $C$. For CH$_3$O in the spectral region studied in this paper, it is reasonable to make the assumptions that if a molecule absorbs a photon it will necessarily
reemit a photon (unity quantum yield) and this photon will be detected with a constant probability. The LIF intensity of a given transition from A to B will then be proportional to the product of the concentration of molecules in initial A state $N_A$ and the strength of transition, $S(A, B)$, from state A to state B,

$$I(A, B) = KN_A S(A, B)$$  \hspace{1cm} (23)

where K is an instrumental constant.

We assume that molecules in the jet are distributed approximately according to the Boltzman distribution at a given temperature $T$ and write the $N_A$ factor as:

$$N_A = \frac{gF(K)e^{-(E_A-E_0)/kT}}{Z}$$ \hspace{1cm} (24)

where $Z$ is a partition function for an ensemble of molecules at a given temperature $T$, $k$ is the Boltzman constant, $g$ is the nuclear spin statistical weight and $E_0$ is the energy of the lowest level belonging to a given type of symmetry. Weber$^{32}$ has considered the problem of nuclear spin weights for a number of symmetric molecules. For the origin of the ground electronic state of CH$_3$O the levels for which $P - \Sigma = 3m + 1 ($m integer$)$ have $a_1$ and $a_2$ rovibronic symmetry with parity $p = \pm 1$ respectively while those for which $P - \Sigma \neq 3m + 1$ belong to $e$ symmetry. The nuclear spin weighting factors are $g = 2$ for each component of $e$ rovibronic symmetry levels and $g = 4$ for the $a_1$ or $a_2$ rovibronic symmetry levels.

Eq. 24 with $F(K) = 1$ corresponds to an equilibrium Boltzman distribution. It has been found that the intensities of most of the lines in the experimental spectra could be satisfactorily simulated with such an equilibrium distribution at temperatures in the range of 4 - 6 Kelvin (depending on the scan) since these lines originate from the rovibronic levels with the quantum numbers $K = 0$ and 1 (which are the lowest levels of a given symmetry). However, some weak progressions in the spectra did not show up in simulations with the equilibrium distribution. To account for these lines the $F(K)$ factor was added to Eq. 24 to reflect the nonequilibrium character of the methoxy ground state distribution in the jet expansion under the experimental conditions of our present work. The intensities of these
progressions may be simulated using the factor $F$ to increase the population of the next higher energy $K$ levels; we found $F(K = -1) \approx F(K = 2) \approx 5 - 10$ depending on the particular spectrum. The values of $F$ vary somewhat in simulations of different experimental spectra which reflects the fact that day by day changes in experimental conditions (photolysis power, amount of sample used etc.) give rise to changes of the population of those stacks.

The values of $S(A, B)$ may be calculated using the eigenfunctions of $\mathcal{H}_{TR}$ obtained for the ground and excited states. We will outline these calculations and as we are particularly interested in $^2a \leftarrow ^2e$ and $^2e \leftarrow ^2e$ vibronic transitions, obtain formulas for them.

Independent of the vibronic symmetry one can write for $S(A, B)$

$$S(A, B) = 3 \sum \langle A \mid d_Z \mid B \rangle^2$$

(25)

where $d_Z$ is the space fixed z component of the dipole moment of the molecule, and $A$ and $B$ denote the quantum numbers which label different eigenfunctions of the ground and excited state Hamiltonian. The summation is over the space-fixed projection quantum in both the $A$ and $B$ states. As any eigenfunction is a linear combination of basis functions in order to calculate $S(A, B)$ it is sufficient to calculate the matrix elements of $d_Z$ in ground and excited state basis vectors and perform the appropriate summation. The operator $d_Z$ corresponds to the $0^{th}$ component of a first rank irreducible tensor operator in a space fixed coordinate system which is related to the corresponding components, $d_r$, in the molecular fixed system by

$$d_Z = \sum_{r=0\pm 1} D_{0r}^1(\omega) \cdot d_r$$

(26)

where $D_{0r}^1(\omega)$ is the rotational matrix relating the molecule and space fixed systems through the Euler angles $\omega$.

For a $^2a \leftarrow ^2e$ transition basis function Eqs. 13 and 20 are used for states $A$ and $B$ respectively. By symmetry the only non-vanishing matrix elements, $M_1$, between $e$ and $a$ vibronic states are:

$$M_1 = \langle e_{\pm} \mid d_{\pm 1} \mid a \rangle$$

(27)
This equation reflects the fact that only perpendicular transitions, i.e., transitions driven by the x and y components of the dipole moment operator, are allowed between $e$ and $a$ vibronic states.

The quantity $S_{a\rightarrow e}(A, B)$, where $a \leftrightarrow e$ denotes a transition between the $e$ and $a_1$ vibronic state, has been evaluated previously\textsuperscript{11} with the result

$$S_{a\rightarrow e}[\{e, J, P, \Sigma, p\}, \{a, J', N', K', p'\}] =$$

$$\delta_{p,-p'}(2J + 1)[J' + (-1)^\gamma(\Sigma - P) + (-1)^\gamma + \frac{1}{2}] \left| M_1 \right|^2 \begin{pmatrix} J & 1 & J' \\ -P & 1 & P' = K + \Sigma \end{pmatrix}^2$$

where $\gamma = 1$ or 2 corresponding to $N = J - 1/2$ and $N = J + 1/2$ respectively for $K \neq 0$.

In addition

$$S_{a\rightarrow e}[\{e, J, P, \Sigma, p\}, \{a, J', N', K' = 0, p'\}] =$$

$$\delta_{p,-p'}(2J + 1)(2J' + 1) \left| M_1 \right|^2 \begin{pmatrix} J & 1 & J' \\ -(1 + \Sigma) & 1 & \Sigma \end{pmatrix}^2$$

for $K = 0$.

Consider now a $^2e \leftrightarrow ^2e$ transition. The $C_{3v}$ symmetry allows the following non-vanishing dipole moment matrix elements between $e$ and $e$ vibronic states:

$$M_1 = \langle e_{\pm} | d_{\pm 1} | e_{\pm} \rangle$$

$$M_0 = \langle e_{\pm} | d_0 | e_{\pm} \rangle$$

These equations reflect the fact both perpendicular and parallel transitions are symmetry allowed for an $e - e$ vibronic symmetry transition.

The value of $S_{e\rightarrow e}(A, B)$ may be calculated directly using the explicit form of the basis function from Eq. (13) and angular momenta coupling techniques with the result

$$S_{e\rightarrow e}[\{e, J, P, \Sigma, p\}, \{e, J', P', \Sigma', p'\}] =$$

$$\delta_{p,-p'}\delta_{\Sigma,-\Sigma'}(2J + 1)(2J' + 1) \left| M_1 \right|^2 \begin{pmatrix} J & 1 & J' \\ -P & -1 & -P' \end{pmatrix}^2$$
for perpendicular transitions and

\[ S_{e\rightarrow e}[(e, J, P, \Sigma, p), (e, J', P', \Sigma', p')] = \delta_{p,-p'} \delta_{\Sigma,\Sigma'} (2J + 1)(2J' + 1) \left| M_0 \right|^2 \begin{pmatrix} J & 1 & J' \\ -P & 0 & P' \end{pmatrix}^2 \]

for parallel transitions. Combination of Eqs. 23, 24, 32 and 33 yield the intensities of individual rotational lines in our simulations.

**B. Results of the rotational analysis**

Two important goals are realized in the rotational analysis. First, the reliability of the assignment of the vibrational bands observed in the LIF spectrum of methoxy can be significantly increased by rotationally fitting the different observed bands. Second, a good deal of information can be obtained about the variation of the rotational and Coriolis parameters as a function of vibrational level.

For purposes of vibrational assignments for methoxy, there are three basic types of transitions observed in the spectrum: those involving totally symmetric modes, fundamentals of \( e \) symmetry vibrations and those involving transitions to levels with 2 quanta of \( e \) motion. Each of these types of transitions has significantly different rotational signatures, and indeed there are even significant sub-classes within the original categories. Upon obtaining a rotational fit for each type of transition it is relatively straightforward to assign most of the vibrations in the LIF spectrum. The following section summarizes the rotational assignments for the different types of vibronic transitions. The rotational constants used for the ground state are taken from previous work\(^{11}\) and are shown in Table IV. Only a few of the parameters previously used are required to fit the spectra to experimental error.
1. Transitions to totally symmetric modes

Transitions in the methoxy radical to \( a_1 \) vibronic levels of the \( \tilde{A}^2A_1 \) state have been rotationally analyzed before. Liu et al.\(^{11}\) analyzed and fit the \( 0^0_0 \) and \( 3^1_0 \) transitions. In the present work the transitions to the \((\nu_3 + \nu_2)^m\) vibrational modes with \( m \) up to 6 have been analyzed. Under our experimental conditions we needed only \( A' \) and \( B' \) rotational constants for the \( \tilde{A} \) state to fit the rotational spectra within experimental error. Fig. 2 shows a typical experimental spectrum with a simulation for the \( 3^2_0 \) transition. The rotational temperature obtained from the intensity fit is 5K for this spectrum with nonequilibrium factors \( F(K=-1)=F(K=2)=5 \). The total number of rotational lines in a band is typically about 20 with a fit residual of 0.04 cm\(^{-1}\). Table V contains the \( A' \) and \( B' \) values for all analyzed transitions for this progression. It should be mentioned that all bands of this type have a very similar rotational contour and the fit is straightforward. Moreover it is possible to identify the band for assignment purposes as belonging to this kind of transition by visual analysis of the contour without actual fitting. However the rotational constants vary significantly from band to band and this variation is discussed in Section V.

2. Transitions to fundamentals of \( e \) symmetry vibrations

The \( e \) vibration is characterized by both its number of quanta \( v \) and the projection of its vibrational angular momentum \( l \). For one quantum of \( e \) vibration there are two degenerate vibrational functions \( |v = 1, l = 1\rangle \) and \( |v = 1, l = -1\rangle \). Multiplied by the electronic \( |A\rangle \) function they serve as the two components, \( |e_\pm\rangle \), of an \( e \) vibronic state as defined in Section IV A 1.

Using the theoretical framework from the previous section it is possible to fit all three \( e \) modes, \( \nu_4 \), \( \nu_5 \), and \( \nu_6 \) and their combinations with symmetric modes. For a nondegenerate electronic state, the average value of the electronic angular momentum \( L_z \) within an \( e \) vibronic state is 0 and hence the first order spin orbit interaction term from Eq. 18 vanishes.
As a result each transition to one quantum of $e$ mode is characterized by two rotational constants, $A'$ and $B'$ and Coriolis interaction constant, $A'\zeta$.

Fig. 4 shows LIF experimental and simulated spectrum of the band, which is assigned to a combination $3_0^24_0^1$ mode. In the previous section it was shown that an $e - e$ symmetry transition may be driven by both the parallel and perpendicular components of the dipole moment operator. Lines observed in the spectrum of Fig. 4 and other transitions involving excitation of quanta of $\nu_4$ require the non-vanishing of both transition dipole components. Table VI contains the rotational and Coriolis constants obtained from the fit of $3_0^14_0^1$ band as well as the relative intensities of the parallel and perpendicular components of the transitions. The rotational constant $A$ is somewhat smaller than for the symmetric modes and the Coriolis constant has a non-zero value $0.46(3)$ cm$^{-1}$. One can see the rotational profile of this band is quite different from ones terminating on $a_1$ modes in the $\tilde{A}$ state. This difference is due to both different rotational selection rules for $a - e$ and $e - e$ transitions and the presence of the Coriolis interaction in $e$ modes.

Fig. 5 shows experimental and simulated spectra of the band assigned as $3_0^15_0^1$. There is a significant difference in the appearance of the $3_0^15_0^1$ band and ones involving excitation of $\nu_4$ or the totally symmetric modes. The difference from the former is due to the absence of parallel transitions in the spectrum and a quite different Coriolis constant. Values for the rotational and Coriolis constants and their variation as the symmetric vibrations are combined with $\nu_5$ are shown in Table VI. The relative intensity of the parallel and perpendicular transitions and the variation in the constants with increasing members of the progressions will be discussed in Section V.

The rotational structure of transitions involving the $\nu_6$ mode is fairly similar to that of those involving $\nu_4$ as Fig. 6 shows for the $3_0^16_0^1$ transition. As in the case of $\nu_4$ both parallel and perpendicular transitions are observed. However, the spectrum is still distinct because the Coriolis constant for $\nu_6$ is quite different from that for $\nu_4$ or $\nu_5$. Table VI also contains rotational and Coriolis constants for analyzed bands containing one quanta of $\nu_6$ excitation.
3. Transitions to Overtones and Combination of e Modes

The structure of transitions to vibronic states with two quanta of e mode excitation is more complex. Three projections of vibronic angular momentum \( l = 2, 0, -2 \) are possible. If the electronic wave function has a symmetry and no vibronic interaction occurs once again one may write the vibronic functions as a product of electronic and vibrational functions:

\[
| e_{\pm} \rangle = | A \rangle | v = 2, l = \mp 2 \rangle \tag{34}
\]

\[
| a \rangle = | A \rangle | v = 2, l = 0 \rangle \tag{35}
\]

where the symbols are consistent with our previous usage.

One should note that the vibrational angular momentum components \( l = \pm 2 \) correspond to the \( |e_{\pm} \rangle \) vibronic function in contrast to those for fundamentals where \( |e_{\pm} \rangle \) corresponds to \( l = \pm 1 \). This choice for the vibronic \( |e_{\pm} \rangle \) functions are required by the transformation properties of Eqs. 10 and 11. In reviewing the literature one sees reported values of Coriolis constants for overtones of e symmetry bands which are twice as large and of opposite sign as for those of the fundamentals. These results represent the empirical (fit) values. The actual Coriolis constants must be calculated by making the adjustment of the signs of the vibrational angular momentum and noting that \(|l| = 2\) not 1. If these adjustments are made the sign and magnitude of the fit Coriolis constant, \( A'\xi_l \), for two quanta overtones of e mode become consistent with that of the fundamental.

Since the e symmetry overtones have both e and a substates, the observed band must be simulated as a combination of \( e - e \) and \( a - e \) vibronic transitions. The simulation of observed spectra show that the origins of the \( e - e \) and \( e - a \) subbands are shifted by several wavenumbers. The nature of this shift may be understood by the following arguments. The degeneracy of the e and a sublevels is only approximate. The complete vibronic Hamiltonian contains a number of interaction terms which lift this degeneracy: the rovibronic interaction term \( A\tilde{G}_z^2 \), anharmonicity from higher order terms of the potential...
energy and general vibronic interactions mixing the $^2A$ electronic state with neighboring $e$ symmetry electronic states. These interactions do not depend upon the rotational quantum number and thus produce a shift of the origins of the $e$ and $a$ vibronic substates.

Fig. 7 shows a spectrum assigned to the $6^2_0$ band, and its simulation as a combination of two subbands, due to $e-e$ and $a-e$ transitions respectively. Both the $e-e$ and $e-a$ transitions were simulated with the same upper state $A'$ and $B'$ constants. For the $e-e$ transition the upper state Coriolis constant $A'_t\xi_t$ was determined in addition to $A'$ and $B'$. Given the equilibrium distribution at $T=4K$ the spectra would be too cold to determine the $A'$, $B'$ and $A'_t\xi_t$ constants simultaneously from a fit of the $e-e$ type subband alone. However, weak progressions due to nonrelaxed $K=-1$ and $K=2$ stacks ( $F(-1)=7$, $F(-2)=15$ ) were observed and allowed the determination of all three constants from the $e-e$ transition and $A'$ and $B'$ constants independently from the $e-a$ transition. A feature to be noted is that unlike fundamentals of $e$ modes which have perpendicular type transitions the observed $e$ overtones and combinations have only parallel ones.

The origins of these two subbands are shifted by a value $T=3.6 \text{ cm}^{-1}$. The rotational constants for analyzed members of the progression are in Table VI. The Coriolis constants for the $6^2$ and $3^16^2$ band are fairly close ($A'_t\xi_t = 0.50(2) \text{ cm}^{-1}$) and quite similar to that of the $6^3_0$ band ($A'_t\xi_t = 0.61(1) \text{ cm}^{-1}$).

A similar structure of the spectra is observed for $5^16^1$ and $5^2$ bands. However the poor S/N ratio and low temperature made it difficult to obtain the rotational constants for these bands.

V. DISCUSSION

In our introduction, we implied that a major motivation for the present work was simply to create a “catalogue” of assigned vibronic levels of the $\tilde{A}^2A_1$ state as a foundation for other experiments. These other experiments include monitoring of CH$_3$O in various chemical reactions of considerable practical importance such as combustion and atmospheric pollution.
Additionally such a “catalogue” is necessary to probe the mode selective photofragmentation process in the $\bar{A}$ state as we have done.\textsuperscript{24} Similarly, identification of the initial vibronic state is critical to the understanding of experiments such as dispersed fluorescence or SEP designed to probe the $\bar{X}$ state structure. Table I essentially fulfills the requirements of this catalogue.

However, beyond assembling this catalogue the present experiments give considerable information about the nature of the $\bar{A}$ state. In particular, rotational analysis of the origins and occasionally a couple of other totally symmetric levels have now been performed for several molecules of methoxy’s general size. Information on the rotational structure of non-totally symmetric levels is much rarer to the point of non-existence, in part of course because transitions to such levels are nominally forbidden. For these reasons it is appropriate to review the information about molecular parameters that we have obtained for the $\bar{A}$ state and see to what conclusions it leads.

Consider first the molecular parameters for the totally symmetric levels. As Table V shows there is a clear decrease in the $B'$ constant as the vibrational energy of CH$_3$O is increased. This trend is certainly expected based upon the stretching of the bonds as the vibrational excitation is increased. Presumably the quite large variation (nearly 10% decrease in $B'$), is attributable at least in part to the continued weakening and lengthening of the C-O bond as the radical tends towards dissociation.

We also see quite a bit of seemingly random variation in the rotational constants within the components of a given Fermi multiplet and, particularly $A'$, from one Fermi multiplet to another. Geometrically in a $C_{3v}$ molecule like CH$_3$O, $A'$ is entirely determined by the positions of the H’s. It appears unlikely that they would be sufficiently displaced towards the $C_3$ axis in the higher vibrational levels to give rise to the observed increase in the $A'$ values. A more probable explanation would be that these are effective $A'$ values, perturbed by Coriolis interactions. As Hougen\textsuperscript{33} showed a number of years ago, the interaction of $a_1$ and $a_2$ vibronic levels can produce just such effective (perturbed) $A'$ constants, in the limit where the perturbation is still relatively weak. (Indeed we have already suggested in Section
III D that stronger Coriolis perturbations may explain the unusual rotational structure of the small number of bands that we have not rotationally analyzed. The perturbing \( a_2 \) vibronic levels may be \( a_2 \) vibrational levels (combination bands or second or higher overtones of \( e \) modes) within the \( \bar{A} \ A_1 \) electronic state. They could also be perturbations from other electronic states particularly the \( 2A_2 \) one in the vicinity. Similar effects should also be possible for the \( B' \) rotational constants, but in this case the perturbing states should be of \( e \) vibronic symmetry.

The rotational constants in Table VI for the \( e \) vibronic levels show similar behavior. There is a gradual decrease in the \( B' \) values as expected but in addition there are significant, relatively random, fluctuations among the constants, particularly the \( A' \) values. Again we expect the cause of these variations is associated with relatively small Coriolis perturbations.

For \( e \) modes of methoxy in addition to \( A' \) and \( B' \), the Coriolis constant \( A'\xi_i \) is determined from the rotational analysis of the spectrum. When the observed Coriolis constant is interpreted as a matrix element over the vibronic functions of a complex operator of vibrational angular momentum there exists a rule\(^{34} \) which relates the sum of the Coriolis constants of all the \( e \) modes in the molecule and the rotational constants,

\[
\xi_{t4} + \xi_{t5} + \xi_{t6} = \frac{B}{2A} \tag{36}
\]

We evaluate the sum rule by writing

\[
A'\xi_{t4} + A'\xi_{t5} + A'\xi_{t6} = \frac{B'}{2} \tag{37}
\]

and use the molecular parameters associated with the lowest vibration observed for a given mode (since these parameters vary from level to level). The evaluation of Eq. 37 leads to the following result:

\[
A'\xi_{t4} + A'\xi_{t5} + A'\xi_{t6} = 0.33(5) \tag{38}
\]

\[
\frac{B'}{2} = 0.37(1) \tag{39}
\]
Clearly these values overlap within the experimental errors. However, referring to Table VI, we see that there is considerable variation in the value of $\xi_{16}$ for the various combination bands involving 5$^1$ and to a lesser extent 6$^1$. In general, there is a clear decrease in $\xi_{15}$ for the more energetic combinations with 5$^1$. While there may be some slight shifting of the inertial axes in the higher combination levels, this would appear to be insufficient to explain the observed effect. Again, we expect Coriolis perturbations play a significant role mixing $a$ and $e$ vibronic states.

The intensities of the rotational transitions provide evidence indicating admixture of an $E$ electronic state into the $e$ vibronic levels of the $\tilde{A}$ state. As described in Section IV A on symmetry grounds the $e - e$ transition is allowed for both perpendicular and parallel transition moments. Moreover, the Jahn-Teller effect in the degenerate $\tilde{X}$ state is usually considered the mechanism by which $e - e$ transitions gain intensity. However a more detailed consideration of the structure of the ground states is worth considering. All transitions in our spectra arise from the vibrationless level of the $\tilde{X}$ state and its wavefunction, including Jahn-Teller effect, may be symbolically written as

$$| e, j = \pm 1/2 \rangle = \sum_i C_i | E_\pm \rangle | v_i, l = \pm 1 \rangle + \sum_k C_k | E_\mp \rangle | v_k, l = 0 \rangle$$

(40)

where $j$ is a quantum number (conserved for a linear Jahn-Teller effect) defined as

$$j = \sum_i l_i - \Lambda / 2$$

(41)

where $l_i$ is the vibrational momentum projection of $e$ mode $i$ and $\Lambda = \pm 1$ for the $|E_\pm\rangle$ electronic functions. In addition, truncating the dipole operator expansion at its first term as is usual, we can write for the transition matrix element $M$,

$$M_{e1} = \langle E_\mp | d_{\mp1} | A \rangle = \langle E_\pm | d_{\pm1} | A \rangle = \langle E_\mp | d_{\mp1} | A \rangle$$

(43)
Thus only perpendicular transitions are expected to be allowed since only the perpendicular part of the dipole moment operator has nonzero matrix elements between electronic states of $a_1$ and $e$ symmetry.

However this conclusion is in a sharp contrast with the experimental observations (Table VI) which indicate that for bands involving fundamentals of $e$ modes, both parallel and perpendicular transitions have been observed with comparable intensities. Further contradictions appear in the $6^2$ overtones. Eq. 40 shows that the linear Jahn Teller effect may mix only vibrational levels with $l = 0$ and $l = \pm 1$ into the lowest $j=1/2$ vibrationless level. As a result the Franck-Condon factor from Eq. 42 will be non-zero only for transitions from the origin to vibrational states with $l = 0, \pm 1$ and as a result transitions to the $e$ component of $6^2$ (which correspond to $l=\pm 2$) should not be allowed. However the $e$ component of $6^2$ is observed and has an intensity 3 times greater than the $a_1$ component (Table VI). These contradictions indicate that the simple picture outlined in Eq. 42 is not correct.

The way to remove this discrepancy is again to assume electronic state mixing. Either the origin of the ground electronic state is mixed with an electronic state of $a_1$ symmetry or the excited $^2A_1$ electronic state is mixed with a nearby electronic state of $e$ symmetry. It seems less probable that the energetically well separated ground $^2E$ state will interact and mix considerably with other states. In contrast the first excited $^2A_1$ state is located near a set of other electronic states as confirmed by computations and recent experiments and it is quite possible that a fairly strong mixing occurs. If one assumes the latter mechanism then the wave function of the fundamental and overtone of the $e$ mode should be symbolically written as

$$| e_A^\pm, v_e^{1} \rangle = \langle 0 | A | v, l = \pm 1 \rangle + \sum_i C_i | E_\pm \rangle | v_i, l = 0 \rangle + \sum_k C_k | E_\mp \rangle | v_k, l = \pm 2 \rangle \quad (44)$$

$$| e_A^\pm, v_e^{2} \rangle = \langle 0 | A | v, l = \pm 2 \rangle + \sum_i C_i | E_\pm \rangle | v_i, l = \pm 1 \rangle + \sum_k C_k | E_\mp \rangle | v_k, l = \pm 3 \rangle \quad (45)$$

where the only requirement placed on the perturbation is that it conserve vibronic symmetry.

The direct substitution of Eqs. 44 and 45 into Eq. 42 shows that all observed transitions can be explained. Thus the rotational analysis provides evidence consistent with the first
excited electronic state of the methoxy radical being considerably mixed with other states, with the $e$ vibrations being promoting modes.

Finally, it should be noted that an earlier SEP experiment\textsuperscript{22} provided evidence for the existence of a parallel transition moment in the $A - \tilde{X}$ spectrum of methoxy. However in that case, the perturbation was suspected to be between the $\tilde{X}$ and $A$ states. While our evidence is not conclusive, we prefer to believe that the $A$ state is being perturbed by excited $E$ states. Independent of that nuance, these experiments have clearly demonstrated that the Jahn-Teller effect in the $\tilde{X}$ state is not solely, or probably even dominantly, responsible for the presence of $e$ vibrational modes in methoxy’s $A - \tilde{X}$ electronic spectrum.

\section*{VI. CONCLUSIONS}

An extensive analysis of the LIF excitation spectrum of the CH$_3$O free radical has been completed. Over 75 vibronic levels of the $\tilde{A}^2A_1$ electronic state have been assigned with a very high degree of reliability, based upon rotational analyses and other evidence. Rather complete analyses of the vibrational frequencies, including a detailed treatment of the strong Fermi resonance involving the $\nu_2$ and $\nu_3$ vibrations, have been carried out. This data constitute a “catalogue” of considerable utility for this most important, and theoretically interesting, free radical.

The rotational analysis of a large number of vibrational bands gives an unusually large database of rotational and Coriolis parameters for the excited $\tilde{A}^2A_1$ electronic state. This data, along with band intensity information, is strongly indicative of significant perturbations of the vibronic levels both from within the $\tilde{A}$ state and by other electronic states in the vicinity.

\textbf{ACKNOWLEDGEMENTS:} The authors gratefully acknowledge support of this work by the National Science Foundation via grant 9320909.
TABLE I. Vibrational frequencies (cm$^{-1}$) and assignments for the $\tilde{X} \ ^2A_1$ state of methoxy

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Position</th>
<th>Assignment</th>
<th>Position</th>
<th>Assignment</th>
<th>Position</th>
<th>Assignment</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>0$^0$</td>
<td>0$^a$</td>
<td>3$^1$</td>
<td>3$^2$</td>
<td>3$^4$</td>
<td>3$^2$</td>
<td>3$^4$</td>
<td>4$^2$</td>
</tr>
<tr>
<td>3$^1$</td>
<td>662.4</td>
<td>3$^1$</td>
<td>3$^2$</td>
<td>3$^4$</td>
<td>3$^2$</td>
<td>3$^4$</td>
<td>4$^2$</td>
</tr>
<tr>
<td>6$^1$</td>
<td>929.5</td>
<td>6$^1$</td>
<td>929.5</td>
<td>6$^1$</td>
<td>929.5</td>
<td>6$^1$</td>
<td>929.5</td>
</tr>
<tr>
<td>2$^1$</td>
<td>1289.3</td>
<td>2$^1$</td>
<td>1289.3</td>
<td>2$^1$</td>
<td>1289.3</td>
<td>2$^1$</td>
<td>1289.3</td>
</tr>
<tr>
<td>3$^2$</td>
<td>1319.3</td>
<td>3$^2$</td>
<td>1319.3</td>
<td>3$^2$</td>
<td>1319.3</td>
<td>3$^2$</td>
<td>1319.3</td>
</tr>
<tr>
<td>5$^1$</td>
<td>1403.0</td>
<td>5$^1$</td>
<td>1403.0</td>
<td>5$^1$</td>
<td>1403.0</td>
<td>5$^1$</td>
<td>1403.0</td>
</tr>
<tr>
<td>3$^4$</td>
<td>1572.9</td>
<td>3$^4$</td>
<td>1572.9</td>
<td>3$^4$</td>
<td>1572.9</td>
<td>3$^4$</td>
<td>1572.9</td>
</tr>
<tr>
<td>6$^2$ (a)</td>
<td>1843.0</td>
<td>6$^2$ (a)</td>
<td>1843.0</td>
<td>6$^2$ (a)</td>
<td>1843.0</td>
<td>6$^2$ (a)</td>
<td>1843.0</td>
</tr>
<tr>
<td>6$^2$ (e)</td>
<td>1846.6</td>
<td>6$^2$ (e)</td>
<td>1846.6</td>
<td>6$^2$ (e)</td>
<td>1846.6</td>
<td>6$^2$ (e)</td>
<td>1846.6</td>
</tr>
<tr>
<td>2$^1$</td>
<td>1935.2</td>
<td>2$^1$</td>
<td>1935.2</td>
<td>2$^1$</td>
<td>1935.2</td>
<td>2$^1$</td>
<td>1935.2</td>
</tr>
<tr>
<td>3$^3$</td>
<td>1971.6</td>
<td>3$^3$</td>
<td>1971.6</td>
<td>3$^3$</td>
<td>1971.6</td>
<td>3$^3$</td>
<td>1971.6</td>
</tr>
<tr>
<td>3$^4$</td>
<td>2065.0</td>
<td>3$^4$</td>
<td>2065.0</td>
<td>3$^4$</td>
<td>2065.0</td>
<td>3$^4$</td>
<td>2065.0</td>
</tr>
<tr>
<td>2$^1$</td>
<td>2196.1</td>
<td>2$^1$</td>
<td>2196.1</td>
<td>2$^1$</td>
<td>2196.1</td>
<td>2$^1$</td>
<td>2196.1</td>
</tr>
<tr>
<td>3$^5$</td>
<td>2217.0</td>
<td>3$^5$</td>
<td>2217.0</td>
<td>3$^5$</td>
<td>2217.0</td>
<td>3$^5$</td>
<td>2217.0</td>
</tr>
<tr>
<td>5$^1$</td>
<td>2321.3</td>
<td>5$^1$</td>
<td>2321.3</td>
<td>5$^1$</td>
<td>2321.3</td>
<td>5$^1$</td>
<td>2321.3</td>
</tr>
<tr>
<td>5$^1$ (e)</td>
<td>2323.8</td>
<td>5$^1$ (e)</td>
<td>2323.8</td>
<td>5$^1$ (e)</td>
<td>2323.8</td>
<td>5$^1$ (e)</td>
<td>2323.8</td>
</tr>
<tr>
<td>3$^6$ (a)</td>
<td>2464.2</td>
<td>3$^6$ (a)</td>
<td>2464.2</td>
<td>3$^6$ (a)</td>
<td>2464.2</td>
<td>3$^6$ (a)</td>
<td>2464.2</td>
</tr>
<tr>
<td>3$^6$ (e)</td>
<td>2468.2</td>
<td>3$^6$ (e)</td>
<td>2468.2</td>
<td>3$^6$ (e)</td>
<td>2468.2</td>
<td>3$^6$ (e)</td>
<td>2468.2</td>
</tr>
<tr>
<td>2$^1$</td>
<td>2558.2</td>
<td>2$^1$</td>
<td>2558.2</td>
<td>2$^1$</td>
<td>2558.2</td>
<td>2$^1$</td>
<td>2558.2</td>
</tr>
<tr>
<td>3$^4$</td>
<td>2618.4</td>
<td>3$^4$</td>
<td>2618.4</td>
<td>3$^4$</td>
<td>2618.4</td>
<td>3$^4$</td>
<td>2618.4</td>
</tr>
<tr>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
</tr>
<tr>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
</tr>
<tr>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
</tr>
<tr>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
<td>2$^1$</td>
<td>2691.1</td>
</tr>
</tbody>
</table>
To obtain the absolute frequency to the effective origin (see text) of each vibrational band, add 31644.2 cm\(^{-1}\) to the relative frequency given above.

Rotational structure not analyzed. See text for possible assignments.
TABLE II. Assignments, frequencies (cm$^{-1}$) and basis function coefficients (derived from the fit to calculations) for the members of the Fermi multiplets

<table>
<thead>
<tr>
<th>multiplet$^a$</th>
<th>Assign.</th>
<th>$\exp.$</th>
<th>$\text{calculated}$</th>
<th>Basis functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\nu_2 + \nu_3)^2$</td>
<td>$2^1$</td>
<td>1289.3</td>
<td>1289.9</td>
<td>$2^03^m$</td>
</tr>
<tr>
<td></td>
<td>$3^2$</td>
<td>1319.3</td>
<td>1320.3</td>
<td>-0.94</td>
</tr>
<tr>
<td>$(\nu_2 + \nu_3)^3$</td>
<td>$2^13^1$</td>
<td>1935.2</td>
<td>1935.7</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>$3^3$</td>
<td>1971.6</td>
<td>1972.9</td>
<td>-0.84</td>
</tr>
<tr>
<td>$(\nu_2 + \nu_3)^4$</td>
<td>$2^2$</td>
<td>2579.2</td>
<td>2580.0</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>$2^13^2$</td>
<td>2558.2</td>
<td>2559.6</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>$3^4$</td>
<td>2618.4</td>
<td>2619.4</td>
<td>0.71</td>
</tr>
<tr>
<td>$(\nu_2 + \nu_3)^5$</td>
<td>$2^23^1$</td>
<td>3216.3</td>
<td>3218.1</td>
<td>-0.62</td>
</tr>
<tr>
<td></td>
<td>$2^13^3$</td>
<td>3259.7</td>
<td>3261.8</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>$3^5$</td>
<td>3181.2</td>
<td>3183.0</td>
<td>0.54</td>
</tr>
<tr>
<td>$(\nu_2 + \nu_3)^6$</td>
<td>$2^3$</td>
<td>3826.0</td>
<td>3827.6</td>
<td>-0.44</td>
</tr>
<tr>
<td></td>
<td>$2^23^2$</td>
<td>3853.3</td>
<td>3853.7</td>
<td>-0.54</td>
</tr>
<tr>
<td></td>
<td>$2^13^4$</td>
<td>3899.2</td>
<td>3899</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>$3^6$</td>
<td>3793.0</td>
<td>3794.3</td>
<td>0.56</td>
</tr>
</tbody>
</table>

$^a$ Terminology defined in Section III C
TABLE III. Vibrational Frequencies (cm\(^{-1}\)) of \(\tilde{A}\)\(^2\text{A}_1\) CH\(_3\)O

<table>
<thead>
<tr>
<th>Mode</th>
<th>(\omega_0)</th>
<th>(\omega_e)</th>
<th>(\omega_{ex})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2947.8</td>
<td>-(^a)</td>
<td>-(^a)</td>
</tr>
<tr>
<td>2</td>
<td>1289.3(^b)</td>
<td>1313.2(7)(^c)</td>
<td>7.37(25)(^c)</td>
</tr>
<tr>
<td>3</td>
<td>662.4</td>
<td>677.2(4)(^c)</td>
<td>4.64(8)(^c)</td>
</tr>
<tr>
<td>4</td>
<td>3077.8(^d)</td>
<td>-(^a)</td>
<td>-(^a)</td>
</tr>
<tr>
<td>5</td>
<td>1403.0</td>
<td>-(^a)</td>
<td>-(^a)</td>
</tr>
<tr>
<td>6</td>
<td>929.5</td>
<td>951.0(^e)</td>
<td>7.1(^e)</td>
</tr>
</tbody>
</table>

\(^a\) Insufficient transitions were observed for these modes to determine \(\omega_e\) and \(\omega_{ex}\).

\(^b\) Perturbed by Fermi resonance with \(3_0^2\).

\(^c\) Based upon calculation of Fermi resonance (see text). Additional parameters in that calculation are \(\omega_{ex} = 9.86(34)\) cm\(^{-1}\) and \(q_F = 6.92(4)\) cm\(^{-1}\). Quoted errors correspond to one \(\sigma\).

\(^d\) Fundamental not observed. Value calculated by subtracting \(\nu_3\) (662.4 cm\(^{-1}\)) from the frequency of \(3^1\text{A}^1\).

\(^e\) Based upon \(6\text{A}^1\) frequency and average frequency of \(a\) and \(e\) components of \(6^2\).
TABLE IV. Ground state molecular parameters\textsuperscript{a} in cm\textsuperscript{-1} used to simulate the rotational structures

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a\xi_{cd}$</td>
<td>-61.974(70)</td>
</tr>
<tr>
<td>$A''$</td>
<td>5.2059(36)</td>
</tr>
<tr>
<td>$B''$</td>
<td>0.9316825(7)</td>
</tr>
<tr>
<td>$A''\xi_t - \epsilon$</td>
<td>1.7730(36)</td>
</tr>
<tr>
<td>$\epsilon_{aa}$</td>
<td>-1.3533(40)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Values obtained from Liu, et al.\textsuperscript{11}
TABLE V. $\tilde{A}^2A_1$ Molecular parameters in cm$^{-1}$ derived from fit to $a_1$ vibronic level rotational structures

<table>
<thead>
<tr>
<th>Band</th>
<th>$A'$</th>
<th>$B'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^0$</td>
<td>4.981(3)</td>
<td>0.7427(1)</td>
</tr>
<tr>
<td>$3^1$</td>
<td>4.983(7)</td>
<td>0.733(1)</td>
</tr>
<tr>
<td>$2^1$</td>
<td>5.03(2)</td>
<td>0.729(6)</td>
</tr>
<tr>
<td>$3^2$</td>
<td>4.98(2)</td>
<td>0.722(5)</td>
</tr>
<tr>
<td>$2^13^1$</td>
<td>5.02(2)</td>
<td>0.723(5)</td>
</tr>
<tr>
<td>$3^3$</td>
<td>4.99(2)</td>
<td>0.717(6)</td>
</tr>
<tr>
<td>$2^2$</td>
<td>4.99(2)</td>
<td>0.711(5)</td>
</tr>
<tr>
<td>$2^13^2$</td>
<td>5.02(2)</td>
<td>0.719(6)</td>
</tr>
<tr>
<td>$3^4$</td>
<td>4.98(2)</td>
<td>0.710(7)</td>
</tr>
<tr>
<td>$2^23^1$</td>
<td>4.98(4)</td>
<td>0.702(4)</td>
</tr>
<tr>
<td>$2^13^3$</td>
<td>4.97(2)</td>
<td>0.693(5)</td>
</tr>
<tr>
<td>$3^5$</td>
<td>4.98(2)</td>
<td>0.693(5)</td>
</tr>
<tr>
<td>$2^3$</td>
<td>5.05(2)</td>
<td>0.709(4)</td>
</tr>
<tr>
<td>$2^23^2$</td>
<td>4.97(2)</td>
<td>0.692(8)</td>
</tr>
<tr>
<td>$3^6$</td>
<td>5.00(2)</td>
<td>0.691(5)</td>
</tr>
</tbody>
</table>

$^a$ Values obtained from Liu, et al.$^{11}$
TABLE VI. \( \tilde{A}^2A_1 \) Molecular Parameters (cm\(^{-1}\)) and relative parallel (\(M_0\)) and perpendicular (\(M_1\)) transition moments as derived from fits to rotational structure of \(e\) vibronic levels

| Band   | \(A'\)     | \(B'\)     | \(A'\xi_t\) | \(|M_0|^2\) | \(|M_1|^2\) |
|--------|------------|------------|-------------|-------------|-------------|
| \(3^14^1\) | 4.87(4)    | 0.734(10)  | 0.43(2)     | 4           | 1           |
| \(5^1\)    | 4.95(4)    | 0.750(7)   | -0.71(7)    | 0           | 1           |
| \(3^15^1\) | 4.90(4)    | 0.743(8)   | -0.57(5)    | 0           | 1           |
| \(3^25^1\) | 4.93(3)    | 0.723(6)   | -0.66(4)    | 0           | 1           |
| \(2^15^1\) | 4.89(3)    | 0.728(7)   | -0.54(4)    | 0           | 1           |
| \(2^13^15^1\) | 4.75(3)   | 0.716(6)   | -0.45(2)    | 0.2         | 1           |
| \(3^5^1\)  | 4.82(4)    | 0.718(8)   | -0.40(5)    | 0           | 1           |
| \(6^1\)    | 4.94(4)    | 0.730(11)  | 0.61(3)     | 2           | 1           |
| \(2^16^1\) | 4.90(3)    | 0.717(5)   | 0.58(2)     | 2           | 1           |
| \(3^16^1\) | 4.93(2)    | 0.730(5)   | 0.62(1)     | 2           | 1           |
| \(3^26^1\) | 4.91(3)    | 0.709(7)   | 0.57(2)     | 2           | 1           |
| \(6^2\)    | 5.08(4)    | 0.720(10)  | 0.50(3)     | 1           | 0\(^a\)     |
| \(3^16^2\) | 5.05(4)    | 0.714(6)   | 0.50(3)     | 1           | 0\(^a\)     |

\(^a\)For these transitions a value of \(|M_1|^2 = 0.3\) was used to simulate the \(a - e\) component.
FIGURE CAPTIONS

1. Portion (a) of the LIF spectrum of methoxy without the teflon fixture attached to the nozzle for cooling. The same portion (b) of the spectrum with the teflon fixture attached. All the features in the lower trace are due to transitions originating in the vibrationless level of the lower spin state of the molecule. The rotational temperature for the trace with the fixture is slightly warmer (5 K) compared to the trace without the fixture (2 K).

2. Experimental (exp) and simulated (sim) spectra of $3_2^2$ band. The simulation is carried out for a transition with a perpendicular ($\perp$) transition moment to an $a$ vibronic level at $T=5$K. The nonequilibrium factors (see text) used were $F(-1)=5$, $F(2)=5$. The arrow indicates the position of the origin. The rotational constants are given in Table V.

3. Schematic representations of the $a_1$ and $e$ vibrations of methoxy.

4. Experimental (exp) and simulated (sim) spectra of the $3_{0}^{2}4_{0}^{1}$ band. The band is simulated as a superposition of the perpendicular ($\perp$) and parallel ($\parallel$) $e - e$ vibronic subbands (two lower traces). The simulation is carried out at $T=4$K, with the nonequilibrium factors (see text) being $F(-1)=15$, $F(2)=10$. The arrow indicates the position of the origin. The molecular parameters and relative subband intensities are given in the Table VI.

5. Experimental (exp) and simulated (sim) spectra of the $3_{0}^{1}5_{0}^{1}$ band. The simulation with only ($\perp$) transition moment to an $e$ vibronic level is carried out at $T=5$ K. The nonequilibrium factors (see text) used were $F(-1)=15$, $F(2)=10$. The arrow indicates the position of the origin of the band. The molecular parameters used in the simulation are given in the Table VI.

6. Experimental (exp) and simulated (sim) spectra of the $3_{0}^{1}6_{0}^{1}$ band. The band is simulated as a superposition of perpendicular ($\perp$) and parallel ($\parallel$) $e - e$ vibronic subbands
(two lower traces). The simulation is carried out at $T=4\text{K}$ with the nonequilibrium factors (see text) being $F(-1)=15$, $F(2)=7$. The arrow indicates the position of the origin. The molecular parameters and relative subband intensities are given in the Table VI.

7. Experimental (exp) and simulated (sim) spectra of the $6_{0}^{2}$ band (two top traces). The band is simulated at $T=5\text{K}$ as a superposition of both $e-a$ and $e-e$ vibronic subbands (two lower traces), with transition moments as indicated. The nonequilibrium factors (see text) used were the same for both subbands $F(-1)=8$, $F(2)=5$. The lower and higher frequency arrows indicate the positions of the origins of $a-e$ and $e-e$ bands, respectively. The molecular parameters and relative subband intensities for the simulation are given in the Table VI.
REFERENCES


24 D. E. Powers, M. Pushkarsky, and T. A. Miller, to be published.


26 F. Temps, to be published.


28 T. Barckholtz and T. A. Miller, to be published.


