Imaging the “missing” bands in the resonance-enhanced multiphoton ionization detection of methyl radical

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Imaging the “missing” bands in the resonance-enhanced multiphoton ionization detection of methyl radical

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Three small features were uncovered in the (2+1) resonance-enhanced multiphoton ionization spectra of CD₃ produced from a crossed-beam reaction of F+CHD₃ near reaction threshold. Taking the velocity mapped images of these features revealed several well-resolved ringlike structures. By conservation of energy, these spectral features were unambiguously assigned to the “missing” bands of 1₁, 3₁, and 4₁ in the literature. These assignments enable all four modes of excitation of this important radical being detected, which could have significant impact on future dynamics studies of the mode specificity of methyl radical. © 2005 American Institute of Physics.

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I. INTRODUCTION

Methyl radical is arguably one of the most important polyatomic radicals. It stands at a unique position as a prototype for the entire class of alkyl radicals. It is also believed to play a key role in the early stages of hydrocarbon combustion,¹ in the troposphere chemistry,² and in the growth of thin film diamond by chemical vapor deposition methods.³ Because of both its fundamental interest and the practical needs, the methyl radical has been the subject of numerous experimental⁴–¹⁵ and theoretical studies.¹⁶–¹⁸ In particular, there have been extensive efforts focused on the development of various sensitive and selective detection methods for diagnostic purposes.⁴–¹² Among them, the (2+1) resonance-enhanced multiphoton ionization (REMPI) spectroscopy is certainly a viable method and has enjoyed a wide range of applications.⁷–¹⁰ In fact, it has been stated in a review¹⁹ that “Of all the radicals so far detected by REMPI spectroscopy, it is probably the newly identified multiphoton resonances of the methyl radical that have had the greatest impact outside the spectroscopic community.”

Recent years have also witnessed increasingly more dynamics studies that involved methyl radical. REMPI detection, in particular, the (2+1) scheme using the 3p₂ ²A” Rydberg state as the intermediate is often the method of choice.¹⁰–³⁷ Methyl radical has four vibrational modes. The selection rules of multiphoton spectroscopy do not forbid any of them from being detected.⁷,¹⁹ Based on the harmonic approximation, a recent ab initio calculation indeed indicated that the diagonal transitions, e.g., 3₁ in the standard spectroscopic notation, of all four modes should exhibit large Franck–Condon factors in the (2+1) REMPI scheme via the 3p₂ Rydberg state.³⁸ Although it remains unclear how the detection sensitivity alters for different modes of excitation due to the predissociation of the 3p₂ intermediate state, experimentally all reported spectra, in both spectroscopic and dynamics studies, are always dominated by the activities of the v₂ mode (umbrella mode) and the most intense ground vibronic band 0₀. The only exceptions are a few reports on the 1₁ Q band (v₁: symmetric C–H or C–D stretch). In a

II. RESULTS AND DISCUSSION

We used the crossed-beam reactions of F+methane and isotopomers to produce the desired CD₃ and CH₃ radicals.³¹,³² Exemplified in Fig. 1 are a series of REMPI spectra of the methyl radicals near the 0₀ Q band. Using the F+CHD₃ → CD₃+HF reaction, all prominent spectral features shown in Fig. 1(a) for Eᵢ=2.8 kcal/mol can readily be assigned to the rotational branches of the 0₀ vibronic transition of the CD₃ radical. The general appearance is what one would usually see in the literature over this wavelength range. However, as one lowers the collisional energies to near reaction threshold, the rotational features are greatly
suppressed and three bandlike structures pop up, as evidenced in Fig. 1(b) for $E_c = 1.0$ kcal/mol. The shifts of these three bands from the peak of the $0_0^0$ branch are $-52$ cm$^{-1}$, $-35$ cm$^{-1}$, and $+22$ cm$^{-1}$, respectively. Here $-\ldots$ denotes redshift and $+\ldots$ blueshift. On the other hand, when the F + CD$_3$ reaction near threshold ($E_c = 0.39$ kcal/mol) was used as the CD$_3$ source, only two spectral features are seen [Fig. 1(c)]; the origin band and the $-52$ cm$^{-1}$ peak. As reported previously, the reaction at higher collision energies the redshifted peak disappears and the REMPI spectra in this wavelength are again dominated by the rotational lines of the $0_0^0$ band. Clearly, the presence of those extra bands or not has to do with the production methods and the detection sensitivities. Similarly, for the F + CH$_4$ → CH$_3$ + HF reaction near threshold only one extra band is discernible from the REMPI spectrum of CH$_3$ [Fig. 1(e) for $E_c = 0.37$ kcal/mol], in contrast to the higher energy one [Fig. 1(d) at $E_c = 2.45$ kcal/mol]. This extra band has previously been assigned to the $1_1^1$ $Q$ branch of CH$_3$.

The identities of the three extra bands, indicated by $\ast\ldots$, for CD$_3$ were revealed by a time-sliced velocity imaging technique. Experimentally, the reaction products CD$_3$ and CD$_4$ were imaged with the probe laser wavelength fixed at the respective peaks. The results are presented in Fig. 2. Displayed in Fig. 2(a) is the image of the peak at 59 848 cm$^{-1}$ of two-photon energy. Because the energetic of this process [the heat of reaction, ground state vibrational frequencies of CD$_3$ (see Table I), and the collisional energy] are well established, it is straightforward, by energy conservation, to assign the state pair ($v_{CD_3}, v_{DF}$) of the two products to the observed features, as indicated in the figure. When the REMPI laser wavelength was shifted slightly to the peak of $O(3)/R(5)$ were imaged with the probe laser wavelength fixed at the respective peaks. The results are presented in Fig. 2. Displayed in Fig. 2(a) is the image of the peak at 59 848 cm$^{-1}$ of two-photon energy. Because the energetic of this process [the heat of reaction, ground state vibrational frequencies of CD$_3$ (see Table I), and the collisional energy] are well established, it is straightforward, by energy conservation, to assign the state pair ($v_{CD_3}, v_{DF}$) of the two products to the observed features, as indicated in the figure. When the REMPI laser wavelength was shifted slightly to the peak of $O(3)/R(5)$

![Fig. 1](image1.png)  
**FIG. 1.** A series of REMPI spectra of the methyl radical near the $0_0^0$ band. Spectra shown in (a) and (b) are for CD$_3$ produced from the F + CHD$_3$ → CD$_3$ + HF reaction at two collision energies, $E_c = 2.8$ kcal/mol and 1.0 kcal/mol, respectively. The different spectral appearances are quite striking. The panel (c) is also for CD$_3$, but from F + CD$_4$ at $E_c = 0.39$ kcal/mol. The spectral assignments of these bandlike features are based on the images shown in Fig. 2. The panels (d) and (e) are for CH$_3$ from F + CH$_4$ at different collision energies, 2.45 kcal/mol and 0.37 kcal/mol, respectively. The confirmation of the $1_1^1$ band has been demonstrated in Ref. 35, and no other features can be detected in (e). The intensities of the $0_0^0$ branch in (a), (b), and (d) are off-scale, thus broken in half in order to display the weaker features.

![Fig. 2](image2.png)  
**FIG. 2.** (Color) Four raw images of the CD$_3$ products from the F + CHD$_3$ reaction [see Figs. 1(a) and 1(b)]. Shown in (a) is the image when laser frequency was fixed at the $1_1^1$ band ($-52$ cm$^{-1}$) shifted from the $0_0^0$ band of Fig. 1(b). The maximum recoil velocity for a given state pair ($v_{CD_3}, v_{DF}$) of the two products was calculated and shown as the dashed circle. Hence, the identification of the spectral feature is based on conservation of energy. Similarly, (b) is for the $3_1^1$ band ($-35$ cm$^{-1}$) shift at the same $E_c = 1.0$ kcal/mol as the $1_1^1$ image. The power of the imaging spectroscopy is demonstrated in (c) and (d) for $E_c = 2.8$ kcal/mol. The corresponding REMPI spectrum is Fig. 1(a) and the laser frequency was set at $+22$ cm$^{-1}$ and $-52$ cm$^{-1}$ from the peak of the $0_0^0$ band for the $4_1^1$ and $1_1^1$ bands, respectively. Although the spectrum is overwhelmed by the $R(1)$, the O(3)/R(5) lines [Fig. 1(a)], the presence of the $4_1^1$ or $1_1^1$ state can still be revealed in the image shown in (c) or (d). The label (0, 3)$^+_h$ in (c) refers to the formation of that product pair from the reaction with the vibrationally excited CHD$_3$ reagent (the low-frequency modes of $v_3$ and $v_4$ in the beam).

![Table I](table1.png)  
**TABLE I.** Vibrational frequencies and the spectral shifts, all in cm$^{-1}$, in the (2+1) REMPI detection of methyl radicals.

<table>
<thead>
<tr>
<th>State</th>
<th>$v_1(a'_1)$</th>
<th>$v_2(a'_2)$</th>
<th>$v_3(e''')$</th>
<th>$v_4(e'')$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$(F$^2\Sigma^+_g$)$^{a,b}$</td>
<td>2158</td>
<td>458</td>
<td>2381</td>
<td>1026</td>
</tr>
<tr>
<td>Shift from $0_0^0$</td>
<td>$-52$, [O(3)/P(5)]</td>
<td>607, $-35$, [P(3)/P(4)]</td>
<td>$+22$, [R(1)]</td>
<td></td>
</tr>
<tr>
<td>CD$_3$(3$P^3\Pi_1^+$)$^{a,b}$</td>
<td>2106</td>
<td>1065</td>
<td>2346</td>
<td>1048</td>
</tr>
<tr>
<td>CH$_3$(F$^2\Sigma^+_g$)$^{a,b}$</td>
<td>3004</td>
<td>607</td>
<td>3161</td>
<td>1398</td>
</tr>
<tr>
<td>Shift from $0_0^0$</td>
<td>$-73$, [P(4)]</td>
<td>716, $-47$</td>
<td>$+30$</td>
<td></td>
</tr>
<tr>
<td>CH$_3$(3$P^3\Pi_1^+$)$^{a,b}$</td>
<td>2931</td>
<td>1323</td>
<td>3114</td>
<td>(1428)</td>
</tr>
</tbody>
</table>

$^a$Reference 40.

$^b$This work. The overlapped rotational transitions of the $0_0^0$ band are given in bracket. The numbers listed in parenthesis for CH$_3$ are estimated from the isotope shifts of the electronic ground state.
transition (not shown), an identical ring structures was seen but with vastly different intensities: the \((0_0, 2)\) pair becomes more intense than the \((1_1, 2)\) pair. Hence, the REMPI peak with a shift of \(-52 \text{ cm}^{-1}\) from the origin band corresponds to one quantum excitation of the symmetric-stretched \(\text{CD}_3\), namely \(1_1^1\), which overlaps spectroscopically with the \(O(3)/R(5)\) lines of the \(0_0^0\) band. This assignment is at variance with the previous assignment of \(-64 \text{ cm}^{-1}\) shift by Chandler et al.\(^{20}\) and the \(-127 \text{ cm}^{-1}\) shift by Hudgens, DiGiuseppe, and Lin\(^7\) Similarly, the other two bands with \(-35 \text{ cm}^{-1}\) \[\text{Fig. 2(b)}\] and \(+22 \text{ cm}^{-1}\) \[\text{Fig. 2(c)}\] shifts are assigned to the missing \(3_1^1\) and \(4_1^1\) bands, respectively.

Further support of the \(1_1^1\) band assignment came from an attempt using the single-beam approach. In this experiment, a \((\text{photolysis+reaction})\) generation scheme was adapted. The methyl radicals were generated by first photolyzing \(\text{N}_2\text{O}\) by an ArF laser, followed by the subsequent reaction of \(\text{O}\) \((1\text{D})\) \(+\text{CH}_4\) (or \(\text{CD}_4\)) during the supersonic expansion in a gas mixture of \(3\% \text{N}_2\text{O}+22\%\) methane \(+75\%\) He. A portion of the resulted \(\text{CD}_3\) spectrum is shown in Fig. 3. Besides the rotational lines of the \(0_0^0\) transition, the two prominent peaks, redshifted by 52 and 104 \text{ cm}^{-1}, are ascribed to the \(1_1^1\) and \(1_2^2\) vibronic transitions, respectively. Not shown in the figure is another weaker peak redshifted from \(0_0^0\) by 2158 \text{ cm}^{-1} which is exactly what one will anticipate for the \(0_0^0\) band. Unfortunately, due to both the overlap with the rotational lines of the more intense \(0_0^0\) band and perhaps unfavorable production scheme, the identifications of the \(3_1^1\) and \(4_1^1\) bands cannot be certain here. Similarly, features corresponding to the \(1_2^1\) and \(1_2^2\) bands of \(\text{CH}_3\) were also found in the single-beam REMPI search (not shown). The spectral shifts are \(-73\) and \(-154 \text{ cm}^{-1}\), respectively.

In conjunction with the well-established ground state vibrational frequencies,\(^{20}\) the present assignments allow us to complete all four vibrational frequencies of \(\text{CD}_3\) in the \(3\text{p}_z\) Rydberg state. The results are summarized in Table I. Since we were unable to detect any assignable features to the \(3_1^1\) and \(4_1^1\) bands for \(\text{CH}_3\)—despite numerous attempts using various production schemes, only an estimate based on the isotope shift of the ground state, which apparently holds for the \(1_1^1\) band, can be given. We hope that it will aid in narrowing down the spectral range for the future search.

III. SUMMARY

In summary, the long-sought missing bands in the \((2 + 1)\) REMPI detection of \(\text{CD}_3\) are identified in this work. Although the signal in the REMPI spectrum is rather weak and by itself is far from convincing, the accompanied imaging detection provides unequivocal evidence, by virtue of energy conservation, for the spectral assignment. With the spectroscopic information available for all four vibrational modes, one can now explore the mode-specific chemistry of this important radical in many dynamical processes. As demonstrated from this work, if one can detect a REMPI signal, no matter how small it is, one can always acquire its image to reveal more insightful dynamical information. In fact, even if the spectral feature is barely discernible or overlapped with the other transition as is seen in Fig. 1(a) or elsewhere,\(^{21,32}\) its presence and dynamical attributes can still be unraveled by the powerful imaging technique provided that the exact spectroscopic position is known, as shown in Fig. 2(c) or Fig. 2(d). The message of this imaging spectroscopy (or spectroscopy by imaging) should be loud and clear.

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37 A. M. Mebel (private communication).