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# Detection of the tunneling-rotation transitions of malonaldehyde in the submillimeter-wave region

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The tunneling-rotation transitions of malonaldehyde, 43 *a*-type *Q*-branch lines, were observed in the submillimeter-wave region of 643–651 GHz. The proton tunneling splitting in the ground state, $\Delta E_0 = 647\,046.208 \pm 0.019$ MHz, and the interaction constant, $F = 45.8965 \pm 0.0082$ MHz, were determined, as well as the molecular constants for each tunneling sublevel. © *1999 American Institute of Physics.* [S0021-9606(99)02609-4]

## I. INTRODUCTION

Malonaldehyde is of great interest with respect to the transfer of a proton between two oxygen atoms, as shown in Fig. 1. The proton transfer of malonaldehyde is governed by a double minimum potential whose barrier is low enough to allow the proton transfer by the tunneling effect. Due to the tunneling effect, the ground state is split into the doublet $0^+$ and $0^-$, where $0^+$ and $0^-$ denote the lower and upper components of the tunneling sublevels, respectively.

Previous microwave studies[1–4] have reported the observation of pure *rotational* lines within the $0^+$ and $0^-$ states, which exhibit *b*-type spectra. Large residuals, often amounting to several multiples of ten MHz, were found for some rotational lines in the fit, and the irregularity was attributed to the tunneling-rotation interaction between the $0^+$ and $0^-$ states. From the analysis of the perturbation, the proton tunneling splitting in the ground state $\Delta E_0$ (separation between the $0^+$ and $0^-$ states) was derived to be $647\,049 \pm 12$ MHz together with the interaction constant $F = 45.51 \pm 0.04$ MHz.[4] Most recently, the measurements were extended to the sub-mmW (submillimeter-wave) region, 352–898 GHz, with tunable far-infrared (TuFIR) spectroscopy. The molecular constants, including the higher-order centrifugal distortion constants, were reported analyzing the rotational lines with large $J$ and $K_a$ quantum numbers.[5]

Observation of the *tunneling-rotation* transitions which connect the $0^+$ state to the $0^-$ state with the *a*-type selection rule will provide more accurate values for the tunneling splitting $\Delta E_0$ and the interaction constant $F$. In the present communication, we report the first observation of tunneling-rotation transitions between the $0^+$ and $0^-$ states by sub-mmW spectroscopy. So far, 43 *a*-type *Q*-branch lines are identified in the frequency region of 643–651 GHz, thanks to the high sensitivity of the sub-mmW spectrometer, and much-improved values for $\Delta E_0$ and $F$ have been obtained.

## II. OBSERVED SPECTRA AND ANALYSIS

The NAIR terahertz spectrometer employing Russian backward-wave oscillators (BWO)[6] was used for the measurement. The radiation generated by a BWO was detected with a liquid He-cooled and magnetically tuned InSb bolometer. The absorption signal was detected phase sensitively by applying a source frequency modulation of 10 kHz and recorded with the 2 $f$ detection mode. The typical accuracy in frequency measurements was estimated to be better than 50 kHz. The malonaldehyde was synthesized from 1,1,3,3-tertramethoxypropane[7] and used for the measurement after purification by vacuum distillation. The distillation process of the sample was monitored by the rotational spectra of malonaldehyde in the sub-mmW region. The sample pressure filled in an absorption cell (1.3 m in length and 8 cm in diameter) was about 15 mTorr. The linewidths observed were typically 1.0 MHz, mostly due to the Doppler width.

A careful search for the tunneling-rotation lines was performed around the band origin of 647 GHz predicted by the previous works. Finally, 43 tunneling-rotation lines were assigned to the group of *a*-type $Q_{Ka}(J)$ lines, with $J - K_a = 0$, 4, and 5, and with $J$ from 8 to 35. A part of the spectra showing the *Q*-branch band head observed at around 643.8 GHz, assigned to the $J - K_a = 4$ series, is reproduced in Fig. 2. For most of the *Q*-branch lines, *K*-type asymmetry doubling is not resolved. The $Q_{12}(16)$ line, for instance, consists of two components; $0^- \leftarrow 0^+$, $J_{Ka,Kc} = 16_{12,5} \leftarrow 16_{12,4}$, and $16_{12,4} \leftarrow 16_{12,5}$, thus abbreviated to $16_{12} \leftarrow 16_{12}$ in Table I. The line intensities of the tunneling-rotation transitions are relatively weak, roughly one-hundredth of those of the pure rotational *b*-type lines. The observed tunneling-rotation transitions are listed in Table I with their assignments.

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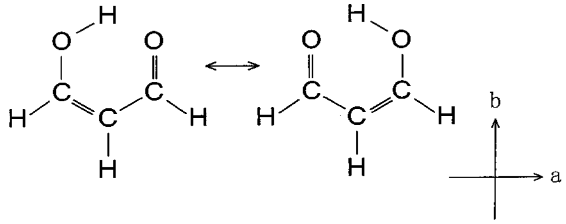


FIG. 1. Configuration of malonaldehyde is illustrated for the two equivalent potential minima with approximate orientation of the molecule-fixed $a$ and $b$ axes.

At first, a number of rather strong pure rotational lines for both the $0^+$ and $0^-$ states were identified in the same frequency region. Thirty-eight rotational lines were newly assigned with the maximum $J$ and $K_a$ quantum numbers of 54 and 37, respectively. The new rotational lines helped to improve the predictions of the line positions and to facilitate the identification of the tunneling-rotation transitions listed in Table I.

These tunneling-rotation line positions and the newly observed 38 pure rotational lines were analyzed together with the rotational transitions for both the $0^+$ and $0^-$ states available in the literature.[1–5] The effective Hamiltonian used for the analysis is essentially the same as in the previous works.[4,5] The large body of data was subjected to a least-squares analysis, in which the present BWO data were weighted to unity, whereas the previous microwave and TuFIR data were weighted typically to 0.1 and 0.01, respectively, referring to their experimental accuracies. The molecular constants are listed in Table II with one standard deviation in parentheses. The standard deviation for the submillimeter-wave lines was about 30 kHz, consistent with the experimental accuracy. The residuals when the interaction constants were set to zero are shown in the last column of Table I, which correspond to the shifts due to the tunneling-rotation interaction.

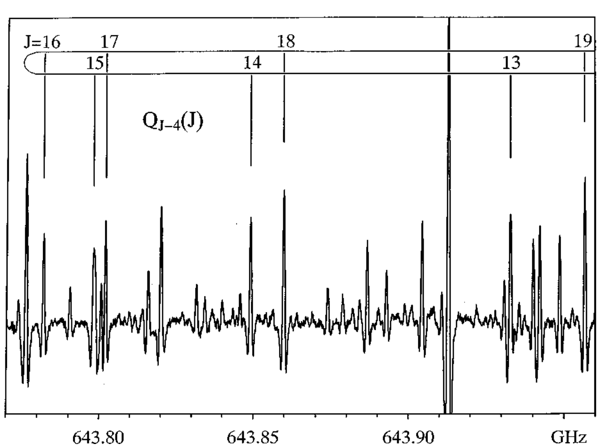


FIG. 2. A portion of the observed spectra of malonaldehyde is reproduced, showing the band head structure of the tunneling-rotation $Q$-branch lines with $J-K_a=4$.

TABLE I. Observed tunneling-rotation transitions of malonaldehyde.[a]

| $0^-$ ← | $0^{+b}$ | Observed | O−C[c] | $\Delta\nu$[d] |
|---|---|---|---|---|
| $10_{10}$ | $10_{10}$ | 647 871.56 | −0.002 | 14.039 |
| $11_{11}$ | $11_{11}$ | 648 092.14 | −0.009 | 18.998 |
| $12_{12}$ | $12_{12}$ | 648 338.22 | −0.004 | 25.045 |
| $13_{13}$ | $13_{13}$ | 648 610.15[e] | 0.240 | 32.309 |
| $14_{14}$ | $14_{14}$ | 648 907.32 | −0.017 | 40.924 |
| $15_{15}$ | $15_{15}$ | 649 230.64 | −0.002 | 51.032 |
| $16_{16}$ | $16_{16}$ | 649 580.00[e] | 0.025 | 62.790 |
| $17_{17}$ | $17_{17}$ | 649 955.52[e] | 0.028 | 76.362 |
| $18_{18}$ | $18_{18}$ | 650 357.39 | 0.025 | 91.925 |
| $8_{4\,4}$ | $8_{4\,5}$ | 647 992.90[e] | −0.376 | 10.515 |
| $9_{5\,5}$ | $9_{5\,4}$ | 643 748.55[e] | 0.205 | 20.883 |
| $10_{6\,5}$ | $10_{6\,4}$ | 644 202.06[e] | 0.038 | 35.932 |
| $10_{6\,4}$ | $10_{6\,5}$ | 644 531.58[e] | −0.049 | 35.917 |
| $11_{7\,5}$ | $11_{7\,4}$ | 644 165.75[e] | 0.015 | 56.665 |
| $11_{7\,4}$ | $11_{7\,5}$ | 644 224.48[e] | 0.582 | 56.660 |
| $12_{8\,5}$ | $12_{8\,4}$ | 644 044.69[e] | 0.020 | 84.051 |
| $12_{8\,4}$ | $12_{8\,5}$ | 644 053.96 | 0.004 | 84.049 |
| $13_{9}$ | $13_{9}$ | 643 932.96[e] | 0.247 | 119.098 |
| $14_{10}$ | $14_{10}$ | 643 849.20 | −0.028 | 162.866 |
| $15_{11}$ | $15_{11}$ | 643 798.46[e] | 0.311 | 216.468 |
| $16_{12}$ | $16_{12}$ | 643 781.99 | 0.002 | 281.081 |
| $17_{13}$ | $17_{13}$ | 643 802.09[e] | 0.031 | 357.957 |
| $18_{14}$ | $18_{14}$ | 643 859.91 | 0.039 | 448.456 |
| $19_{15}$ | $19_{15}$ | 643 956.83 | 0.007 | 553.890 |
| $20_{16}$ | $20_{16}$ | 644 095.58[e] | 0.827 | 676.037 |
| $21_{17}$ | $21_{17}$ | 644 275.42 | −0.008 | 816.622 |
| $22_{18}$ | $22_{18}$ | 644 503.21[e] | −0.012 | 979.992 |
| $23_{19}$ | $23_{19}$ | 644 769.74 | 0.002 | 1157.731 |
| $24_{20}$ | $24_{20}$ | 645 092.80 | −0.025 | 1367.679 |
| $30_{26}$ | $30_{26}$ | 648 142.55 | −0.068 | 3227.048 |
| $31_{27}$ | $31_{27}$ | 648 873.70[e] | −0.002 | 3674.537 |
| $32_{28}$ | $32_{28}$ | 649 677.88 | 0.009 | 4170.806 |
| $12_{7\,6}$ | $12_{7\,5}$ | 643 043.44[e] | −0.076 | 70.750 |
| $12_{7\,5}$ | $12_{7\,6}$ | 643 254.20[e] | 0.089 | 70.735 |
| $24_{19}$ | $24_{19}$ | 643 074.53[e] | −0.346 | 1446.764 |
| $25_{20}$ | $25_{20}$ | 643 374.18 | −0.045 | 1711.758 |
| $26_{21}$ | $26_{21}$ | 643 820.06 | −0.167 | 2099.055 |
| $27_{22}$ | $27_{22}$ | 644 091.61[e] | 0.026 | 2287.345 |
| $28_{23}$ | $28_{23}$ | 644 573.10 | −0.008 | 2661.434 |
| $29_{24}$ | $29_{24}$ | 645 113.18 | −0.012 | 3069.716 |
| $33_{28}$ | $33_{28}$ | 648 016.69 | −0.034 | 5202.508 |
| $34_{29}$ | $34_{29}$ | 648 955.94 | 0.025 | 5888.195 |
| $35_{30}$ | $35_{30}$ | 649 992.80 | 0.008 | 6647.275 |

[a]In MHz units.
[b]$J_{K_aK_c}$; if asymmetry doubling is not resolved, only $J_{K_a}$ is shown.
[c]Observed minus calculated frequencies in MHz.
[d]Shift by the tunneling-rotation interaction.
[e]Not included in the fit because they were either overlapping or weak.

## III. DISCUSSION

The determined tunneling splitting $\Delta E_0 = 647\,046.208 \pm 0.019\,\mathrm{MHz}$ ($21.583\,138\,29 \pm 0.000\,000\,63\,\mathrm{cm}^{-1}$) in the ground state is consistent with the previous microwave result $647\,049 \pm 12\,\mathrm{MHz}$ (Ref. 4) within the error limit. The interaction constant-determined $F = 45.8965 \pm 0.0082\,\mathrm{MHz}$ is also consistent with the previous microwave value, $F = 45.51 \pm 0.04$.[4] The $J$ and $K_a$ dependent terms, $F_J$ and $F_K$, were determined for the first time by this study because of the high quantum numbers of the observed transitions. The interaction effects on the tunneling-rotation frequencies are positive as shown in the last column of Table I, meaning that

TABLE II. Molecular constants of malonaldehyde.[a]

| | $0^+$ state | $0^-$ state | Unit |
|---|---|---|---|
| $A$ | 9833.842 29(92) | 9846.055 69(93) | MHz |
| $B$ | 5212.535 66(64) | 5158.733 75(75) | MHz |
| $C$ | 3404.376 73(81) | 3383.221 10(60) | MHz |
| $\Delta_J$ | 3.905 0(15) | 2.949 0(17) | kHz |
| $\Delta_{JK}$ | −6.414 2(54) | −4.200 5(67) | kHz |
| $\Delta_K$ | 6.911 0(41) | 5.670 2(52) | kHz |
| $\delta_J$ | 1.436 81(75) | 1.062 14(72) | kHz |
| $\delta_K$ | 4.090 2(63) | 3.707 7(91) | kHz |
| $H_J$ | 0.004 3(3) | −0.017 4(3) | Hz |
| $H_{JK}$ | 0.020 5(10) | 0.056 0(16) | Hz |
| $H_{KJ}$ | −0.066 9(22) | −0.083 5(35) | Hz |
| $H_K$ | 0.048 3(14) | 0.049 9(22) | Hz |
| $\Delta E_0$ | 647 046.208(19) | | MHz |
| $F$ | 45.8965(82) | | MHz |
| $F_J$ | 876.6(17) | | Hz |
| $F_K$ | −741.5(34) | | Hz |

[a]The figures in the parentheses are uncertainties ($1\sigma$) in units of the last digit.

the repulsion between the $0^+$ and $0^-$ states increases the energy separation. The interaction amounts to a few multiples of ten MHz when the $J$ and $K_a$ quantum numbers are small, but is as large as 6647.3 MHz for the $35_{30} \leftarrow 35_{30}$ transition. The rotational and centrifugal distortion constants listed in Table II are also consistent with the previous results,[4,5] whereas their accuracies are improved more than one order of magnitude.

The *b*-component of dipole moment, responsible for the pure rotational transitions, has been measured from the Stark effect to be 2.59 and 2.58 *D*, respectively, for the $0^+$ and $0^-$ states.[2] Although the determination of the *a*-component (strictly the transition moment), responsible for tunneling-rotation transitions between the $0^+$ and $0^-$ states, is not easy from the Stark effect, the reported value of about 0.2–0.4 D (Ref. 2) from the isotopic species turns out to be reasonable, considering the line intensities. The tunneling-rotation transitions observed are approximately two orders of magnitude weaker than those of the pure rotational transitions, and the line profile simulation, assuming the ratio ($\mu_a/\mu_b$) of 0.14, reproduces the observed spectrum fairly well.

In conclusion, the tunneling-rotation transitions of malonaldehyde were observed in the submillimeter-wave region, and the proton tunneling splitting in the ground state $\Delta E_0 = 647\,046.208 \pm 0.019$ MHz and the interaction constant $F = 45.8965 \pm 0.0082$ MHz were determined.

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[1] W. F. Rowe, R. W. Duerst, and E. B. Wilson, J. Am. Chem. Soc. **98**, 420 (1976).
[2] S. L. Baughcum, R. W. Duerst, W. F. Rowe, Z. Smith, and E. B. Wilson, J. Am. Chem. Soc. **103**, 6296 (1981).
[3] S. L. Baughcum, Z. Smith, E. B. Wilson, and R. W. Duerst, J. Am. Chem. Soc. **106**, 2260 (1984).
[4] P. Turner, S. L. Baughcum, S. L. Coy, and Z. Smith, J. Am. Chem. Soc. **106**, 2265 (1984).
[5] D. W. Firth, K. Beyer, M. A. Dvorak, S. W. Reeve, A. Grushow, and K. Leopold, J. Chem. Phys. **94**, 1812 (1991).
[6] I. Morino, M. Fabian, H. Takeo, and K. M. T. Yamada, J. Mol. Spectrosc. **185**, 142 (1997).
[7] E. J. J. Grabowski and R. L. Audrey, Tetrahedron **25**, 4315 (1969).