

NEW MEASUREMENTS OF SUB-MILLIMETRE-WAVE ROTATIONAL TRANSITIONS FOR THE
KETENE (H_2CCO) MOLECULE

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Using the superheterodyne sub-millimetre spectrometer at the Micro-wave Laboratory of the University of Lille I, France some hitherto unavailable pure rotational transitions have been measured for the ketene molecule (CH_2CO). The measurements were extended up to almost 800 GHz and contained a-type $\Delta K_a=0$ transitions. These new data were then used in conjunction with cm- and mm-wave transitions reported in the literature, plus various ground-state combination differences recalculated from an earlier high-resolution infrared study of ketene. This data set was used to re-derive ground state rotational constants for ketene both in the A and S reduction scheme of Watson.

Introduction

Ketene is a fairly abundant molecule in interstellar space [1]. Since the available millimetre-wave data for this molecule is restricted to relatively low frequencies [2], i.e. only up to 200 GHz, it has been considered worthwhile to extend the measurements into the high-frequency sub-millimetre-wave spectral range. Another motivation for these studies has been to cast the rotational and centrifugal distortion constants into the recent notation due to Watson [3].

Experimental

Ketene gas was generated from liquid diketene (CH_2CO)₂ in a flow system containing a quartz tube heated to about 600°C. Diketene was first frozen out in a liquid N₂ trap while the spectrometer was pumped down. Then the sample was allowed to warm up in order to distil at a needle-valve controlled rate into the waveguide, wherefrom it was pumped away. Pure ketene could be produced in this way in sufficient quantities.

The sub-millimetre spectrometer used in these studies was described by Burie et al [4]. To find the high-frequency rotational transitions their position was predicted using previously reported ground state constants (see: Johns et al [2]). For this purpose a computer programme written by Dr. Koichi Yamada was used. This procedure facilitated greatly the search for the right ketene line. In the case of the Lille spectrometer this was particularly important since the super-heterodyne detection system applied resulted in very high sensitivity. Once the transition was located its line parameters were measured by the sophisticated data-processing software

developed at the Laboratoire de Spectroscopie Hertzienne in Lille.

Analysis of the spectra

The input data for the least-squares calculation of molecular constants consisted of three subsets: i. cm- and mm-wave lines given in ref. [2], ii. the presently reported measurements of sub-mm-wave lines, and iii. combination differences recalculated from the b-type ν_7 infrared band frequencies in ref. [2]. The distribution of data among the three subsets is as follows: i.:52, ii.:82 and iii.: 278.

The least-squares determination of the ground state rotational constant set was made partly in Lille and partly in Giessen, Justus-Liebig-University, West Germany. In Lille we have used a computer programme written by Dr. V. Typke, adapted to the local DPS8 computer. The Giessen calculations were carried out by another programme originally written by Dr.K. Yamada and later modified by Dr. Brenda Winnewisser for the local computer at the University of Giessen. In this paper only the Giessen calculations shall be reported as they were made on the original Lille data set, but were carried out in both the A- (asymmetric top), and S- (symmetric top) reduction schemes of Watson [3].

Ground state rotational constants of H₂CO

A-reduction

The following rotational Hamiltonian was used in the data fitting procedure:

$$\begin{aligned} \hat{H}_{\text{rot}}^{(A)} = & \tilde{A} \hat{J}_z^2 + \tilde{B} \hat{J}_x^2 + \tilde{C} \hat{J}_y^2 - \Delta_J \hat{J}^4 - \Delta_{JK} \hat{J}^2 \hat{J}_z^2 - \\ & - \Delta_K \hat{J}_z^4 - (1/2) [\delta_J \hat{J}^2 + \delta_K \hat{J}_z^2, (\hat{J}_+^2 + \hat{J}_-^2)]_+ + \\ & + \Phi_J \hat{J}^6 + \Phi_{JK} \hat{J}^4 \hat{J}_z^2 + \Phi_K \hat{J}_z^6 + \\ & + (1/2) [\phi_J \hat{J}^4 + \phi_{JK} \hat{J}^2 \hat{J}_z^2 + \phi_K \hat{J}_z^4, (\hat{J}_+^2 + \hat{J}_-^2)]_+ . \end{aligned} \quad (1)$$

S-reduction

In the S-reduction scheme the Hamiltonian is of the following form:

$$\begin{aligned} \hat{H}_{\text{rot}}^{(S)} = & (\tilde{A} - (\tilde{B} + \tilde{C})/2) \hat{J}_z^2 + ((\tilde{B} + \tilde{C})/2) \hat{J}^2 - D_J \hat{J}^4 - \\ & - D_{JK} \hat{J}^2 \hat{J}_z^2 - D_K \hat{J}_z^4 + H_J \hat{J}^6 + H_{JK} \hat{J}^4 \hat{J}_z^2 + H_{KJ} \hat{J}_z^2 \hat{J}^4 + \\ & + H_K \hat{J}_z^6 + ((\tilde{B} - \tilde{C})/4 + d_1 \hat{J}^2 + h_1 \hat{J}^4) (\hat{J}_+^2 + \hat{J}_-^2) + \\ & + (d_2 + h_2 \hat{J}^2) (\hat{J}_+^4 + \hat{J}_-^4) + h_3 (\hat{J}_+^6 + \hat{J}_-^6). \end{aligned} \quad (2)$$

It is possible to relate the rotational constants in the A- and S-reduction forms (see: Table 8.16 in ref. [5]). Such a comparison was performed among the least-squares determined A-reduction constants and those calculated from S-reduction constants using the relationships in ref. [5]. In addition to this the least-squares errors were checked by error propagation. It was found that the data in Table I and II satisfy such relations

within the calculated error limits. The only exception is $\tilde{\Phi}_{JK}$ that is significantly different from H_{JK} although these constants are expected to be identical in the present constraint: $h_2=h_3=0$.

Table I
Results of the A-reduction fit for
H₂CCO

\tilde{A}	282198.0(71.3)	MHz
\tilde{B}	10293.913(19)	MHz
\tilde{C}	9915.245(19)	MHz
Δ_J	3.3876(52)	kHz
Δ_{JK}	468.73(27)	kHz
Δ_K	30.1(4.6)	MHz
δ_J	0.1463(38)	kHz
δ_K	313.2(9.4)	kHz
$\tilde{\Phi}_{JK}$	3.73(21)	Hz
$\tilde{\Phi}_{KJ}$	-0.9009(46)	kHz

Table II
Results of the S-reduction fit
for H₂CCO

$\tilde{A}-(\tilde{B}+\tilde{C})/2$	272093.0(71.3)	MHz
$(\tilde{B}+\tilde{C})/2$	10104.5791(33)	MHz
$(\tilde{B}-\tilde{C})$	377.4150(27)	MHz
D_J	3.2790(42)	kHz
D_{JK}	469.38(27)	kHz
D_K	300.7(4.6)	MHz
H_{JK}	3.26(21)	Hz
H_{KJ}	-0.8994(46)	kHz
d_1	-0.1463(38)	kHz
d_2	-54.3(1.6)	Hz

The correlations among the A-reduction parameters and those for the S-reduction parameters are significantly different. In the asymmetric top reduction the strongest correlations (>0.9) are between members of pairs: (\tilde{A}, Δ_{JK}) ; (\tilde{A}, δ_K) ; $(\tilde{A}, \tilde{\Phi}_{KJ})$ and $(\delta_K, \tilde{\Phi}_{KJ})$ whereas in the symmetric top reduction $((\tilde{A}-\tilde{B}^*), D_K)$; $((\tilde{A}-\tilde{B}^*), d_2)$ and $((\tilde{B}-\tilde{C}), d_1)$, where $\tilde{B}^* = (\tilde{B}+\tilde{C})/2$.

Although a direct comparison to the results of Johns et al [2] is not possible due to the different notations, it is interesting to note that in the present S-reduction D_K is significantly larger, whereas H_{JK} is significantly smaller than in ref.[2].

Further work is in progress for the more accurate determination of the

ground state rotational constants. Dr. J.W.C. Johns and one of the present authors (L.N.) have recorded Doppler-limited resolution spectra of ketene in the spectral range 1100-350 cm^{-1} using the BOMEM DA3.002 FTIR spectrometer at the Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa. New, highly dependable ground state combination differences have already been derived from the rotational structure of the ν_8 fundamental and these have been used to extend the scope of the present work significantly [6].

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