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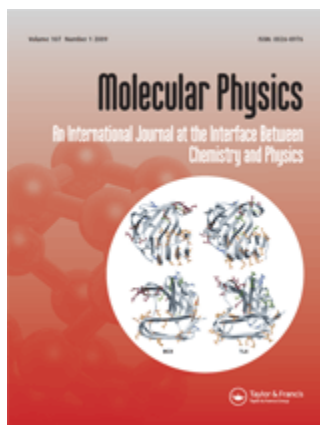
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Global vibration-rotation analysis**

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**The bending vibrations in  $^{12}\text{C}_2\text{H}_2$ :  
Global vibration-rotation analysis**

*Revised version  
John Brown's special issue*

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## Abstract

A total of 3155 vibration-rotation line positions providing accurate information on all known vibration-rotation states up to  $3000\text{ cm}^{-1}$  in  $^{12}\text{C}_2\text{H}_2$  were gathered from the literature. Additional 966 lines were assigned on new spectra. The full data set was simultaneously fitted using an appropriate Hamiltonian, with 85 refined parameters. A dimensionless standard deviation equal to 0.86, accounting for 92 % of the lines, was achieved. The vibrational transition dipole moment of the  $\nu_5 = 1 \leftarrow \nu_4 = 1$  band observed in the far-infrared was estimated to be  $|\mu_{5\leftarrow 4}| = 0.55\text{ D}$  with 20 % accuracy, from absolute intensity measurements for a few  $Q$ -branch lines.

## 1. Introduction

Since the pioneering contribution of Plíva (1, 2), a number of experimental and theoretical studies have concerned the bending vibrations in acetylene,  $^{12}\text{C}_2\text{H}_2$  (1-55). Of particular interest to the present investigation is the global modeling of the bending vibration-rotation levels in  $^{12}\text{C}_2\text{H}_2$ , first performed by Plíva (1, 2) who addressed the problem of  $l$ -type doubling associated to the two degenerate bending vibrations in this species,  $\nu_4$  (*trans*-bending) and  $\nu_5$  (*cis*-bending). This work was later extended by considering additional experimental data and/or terms in the Hamiltonian, by (11, 25-27, 35) and also additional isotopologues of this molecule (56-59). In their contribution on  $^{12}\text{C}_2\text{H}_2$ , Kabbadj et al. (25) achieved a global vibration-rotation fit considering vibration-rotation lines from 43 bands involving bending vibrational states up to  $\sum_b \nu_b \leq 4$ , with  $b$  the bending vibrations, as well as the  $\nu_2 = 1$  vibrational state, with  $\nu_2$  the CC stretch.

We have since accessed to new pure bending vibrational transitions among the same states and to new vibration-rotation lines of previously assigned vibrational transitions, by refining the analysis of the Fourier transform spectra presented in (26). Additional new bands also became available in the literature, at higher energy, either again connecting differently the states previously observed, or involving upper stretch ( $\nu_2$ )-bend combination states not previously considered (53). All these new bands add

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3 relevant information on the pure bend states of interest to the present  
4 investigation. There was therefore room for improving the global vibration-  
5 rotation fit on the bends, which we have performed using a dedicated package  
6 of computer programs. The Hamiltonian and the data set are presented in  
7 section 2 and the results are detailed in section 3. **This contribution is**  
8 **actually part of a much larger effort in the global analysis of the known**  
9 **vibration-rotation data of acetylene, up to the overtone range.**  
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23 The program package allows relative vibration-rotation line intensities  
24 to be predicted accounting for all terms in the energy Hamiltonian. We have  
25 used these facilities to estimate, in section 4, the induced dipole moment of  
26 the  $v_5 = 1 \leftarrow v_4 = 1$  (named  $v_5 - v_4$ ) band observed in the far-infrared (FIR), of  
27 interest to astrophysical detection.  
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## 43 **2. Global Hamiltonian and data set**

44 The previous work on the global fitting of the vibration-rotation lines  
45 in the bending range of acetylene was achieved using the Hamiltonian  
46 defined in (25, 26) and a computer program written at ULB and refined in  
47 Bologna. A different computer program was used in the present work,  
48 developed at Louvain-La-Neuve and dedicated to both energy and intensity  
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3 treatments (60-62). The form of the Hamiltonian is different from the one  
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6 previously used and presented in table 1.  
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11 The initial data set we considered was identical to the one in (25, 26),  
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13 resulting from the analysis of FTIR spectra recorded in Ottawa at the  
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15 Herzberg Institute of Astrophysics. Vibration-rotation lines involving the CC  
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17 stretch,  $\nu_2$ , were observed in the same range as highly excited pure bending  
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19 vibrations, and were also considered at that time. Information on the related  
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21 experimental conditions can be found in (25, 26). The analysis in the spectral  
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23 region around  $500\text{ cm}^{-1}$  was later extended in Bologna. New pure bending  
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25 vibrational transitions as well as additional vibration-rotation lines in  
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27 vibrational transitions previously assigned could be identified in a spectrum  
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29 recorded with longer path length. This spectrum was recorded in Ottawa with  
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31 a modified Bomem DA3.002 FT interferometer, in the  $420 - 580\text{ cm}^{-1}$  range,  
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33 at 333 K, with an absorption path length of 80 m and a sample pressure of  
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35 260 Pa. The instrument was equipped with a Cu-Ge detector cooled to liquid  
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37 He temperature and the achieved resolution was  $0.003\text{ cm}^{-1}$ . Table 2 lists  
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39 this new information. The related line list can be obtained from the Bologna  
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41 authors. The data set presently considered was thus extended to include all  
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43 these additional lines. Besides, vibration-rotation lines reported in (53) from  
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45 a spectrum recorded in a higher energy range compared to the one in (26)  
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47 were also added. They mainly concern hot bands towards higher excited bend  
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49 states as well towards stretch ( $\nu_2$ )-bend combination states.  
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6 The full data set amounts to 4121 vibration-rotation lines, with 2531  
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8 from (26), 966 from assignments performed on the new spectra and 624 from  
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10 (53). All related vibrational transitions are identified in figure 1, which  
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12 updates figure 5 of (26). They are detailed in table 3, which summarizes the  
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14 full data set used in the global fit.  
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### 26 **3. Results**

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28 A weighted least-squares fitting procedure was adopted, accounting for  
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30 the experimental accuracy, estimated to be  $3 \times 10^{-4} \text{ cm}^{-1}$  for the data from (26)  
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32 and for the new data and  $2 \times 10^{-4} \text{ cm}^{-1}$  for those from (53). As usual in such  
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34 procedures, the selection of higher order terms in the model is delicate given  
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36 the high correlation between some of the parameters. We included only those  
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38 higher order constants which seemed most efficient in reducing the standard  
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40 deviation of the fit, while keeping a reasonable value compared to the  
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42 corresponding ones of lower order in the development.  
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51 The fitting procedure led to a set of 85 parameters listed in table 4, with  
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53 dimensionless standard deviation of 0.86 on 3795 fitted lines out of 4121  
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55 assigned transitions. 326 lines presenting anomalously large (obs. – calc.)  
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57 values were excluded from the fit. They correspond to very weak and/or  
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3 blended lines. As already mentioned in (26), a few rejected transitions  
4 probably suggest local Coriolis perturbation effects, which have not been  
5 included in the model Hamiltonian.  
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13 It is interesting to point out that the bending Darling-Dennison  
14 anharmonic resonance 44/55, discussed e.g. in (63), had to be included in the  
15 Hamiltonian defined in table 1 in order to achieve the presently obtained  
16 standard deviation. It could not be previously determined in (26). This  
17 resonance is known to significantly contribute in higher excited ranges of the  
18 vibrational ladder, where the related interacting states are closer in energy.  
19 The accuracy of the present data combined with the inclusion of higher  
20 excited bend states in the procedure, compared to the data set in (26),  
21 explains the need for introducing the 44/55 resonance. The related  
22 parameter,  $|K_{44/55}| = 8.9 \text{ cm}^{-1}$ , is very close the value of  $8.3 \text{ cm}^{-1}$  determined  
23 in (63).  
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43 Compared to previous results (26), more lines are fitted in the present  
44 work (3795 against 2307), as well as more bands. The R.M.S. error on the  
45 lines previously considered is actually much better ( $0.00026 \text{ cm}^{-1}$  compared to  
46  $0.000439 \text{ cm}^{-1}$ ) while the number of determined parameters is similar (85  
47 against 80 previously reported). In fact, 4 of the additional parameters ( $x_{24}$ ,  $x_{25}$ ,  
48  $\gamma_{24}$ ,  $\gamma_{25}$ ) arise from the inclusion of the two stretch-bend states ( $v_2+v_4$  and  $v_2+v_5$ ),  
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not previously considered. All corresponding parameters in the Hamiltonian have very close values in both sets of results.

The resulting vibrational term values are provided in table 5, for each  $k$ -substate. They correspond to calculated rotationless energies,  $G_C$  defined as

$$G_C = G_{v'}^0 - B_{v'} k'^2 - D_{v'} k'^4 \quad (1)$$

with  $k = l_4 + l_5$

#### 4. The $\nu_5$ - $\nu_4$ band

The  $\nu_5$  -  $\nu_4$  FIR band was previously reported in (26) and the 129 observed vibration-rotation transitions were included in the present global fit. This band is of interest for the detection of acetylene in the FIR range, with obvious astrophysical applications (64). The line positions, already included in the Cologne Database (65, 66), see <http://www.ph1.uni-koeln.de/cgi-bin/cdmssearch?file=w026505.cat>, are not repeated here.

As values for absolute intensities would obviously help in this context we decided to estimate the related transition dipole moment,  $|\mu_{5\leftarrow 4}|$ , using existing information. The absolute intensity of  $Q$ -branch lines observed in the range  $117.36 - 117.55 \text{ cm}^{-1}$  was measured by fitting a synthetic spectrum to

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3 the observed transmittance spectrum presented in figure 1 of (26). This  
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5 spectrum was recorded at 294 K, with an absorption path length of 18 m and  
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7 a sample pressure of 100 Pa. The synthetic spectrum was computed by  
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9 application of Beer's law, using a Voigt function to model the observed line  
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11 profiles and including instrumental distortion resulting from the finite  
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13 maximum optical path difference achieved (445 cm) and source aperture  
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15 diameter of the interferometer (2.5 mm). Figure 2 shows the spectra observed  
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17 and calculated at the end of the fit. From the measured absolute line  
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19 intensities, we determined using usual methods (67) the value of the  
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21 vibrational transition dipole moment of the  $\nu_5-\nu_4$  band to be  $|\mu_{5\leftarrow 4}| = 0.55$  D.  
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29 Its accuracy is not expected to be better than 20%.  
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## 39 5. Conclusions

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41 We have gathered all the accurate spectral information observed in the  
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43 lower energy range of the infrared spectrum concerning the bending  
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45 vibration-rotation states on  $^{12}\text{C}_2\text{H}_2$  reported in the literature. During the  
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47 present investigation, new bands and additional vibration-rotation lines in  
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49 some known bands were assigned on new spectra recorded at longer path  
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51 length and included in the data set. A total of 3795 vibration-rotation lines  
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53 were successfully fitted to a set of 85 parameters of a global Hamiltonian.  
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59 They were determined with previously unmatched precision, with a  
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3 dimensionless standard deviation of the fit equal to 0.86. They were used to  
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5 simulate, among others, the  $\nu_5$ - $\nu_4$  FIR band, of astrophysical relevance. The  
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7 comparison with the observed transmittance spectrum of this band allowed  
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9 the related transition dipole moment to be determined.  
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## Figure Legends

**Figure 1.** Vibrational states and transitions in  $^{12}\text{C}_2\text{H}_2$  taken into account in the present investigation, with the following labels: (—) from (26); (- - -) presently newly assigned; (····) from (53). The states are identified with the values of the bend quantum numbers ( $v_4v_5$ ) or with  $v_2+v_{4/5}$  for the stretched combination states.

**Figure 2.** Spectrum of the  $v_5-v_4$  band of  $^{12}\text{C}_2\text{H}_2$  near the band origin, recorded at the National Research Council Canada (Ottawa) and presented in Fig. 1 of (26) ( $T = 294$  K,  $l = 18$  m,  $P = 100$  Pa). In the upper part of the figure, the solid line and the symbols represent respectively the spectra observed and calculated at the end of the fit. The lower part of the figure shows the corresponding residuals.

## Table Captions

**Table 1.** Terms in the Hamiltonian used to perform the global vibration-rotation fit in  $^{12}\text{C}_2\text{H}_2$ .<sup>a</sup>

**Table 2.** Bands of  $^{12}\text{C}_2\text{H}_2$  newly measured.

**Table 3.** Summary of the full data set used in the global vibration-rotation fit of the bending states in  $^{12}\text{C}_2\text{H}_2$ .<sup>†</sup>

**Table 4.** Vibration-rotation parameters in  $^{12}\text{C}_2\text{H}_2$  ( $\text{cm}^{-1}$ ).<sup>a</sup>

**Table 5.** Calculated vibrational term values  $G_c$  ( $\text{cm}^{-1}$ ) of all  $v,l$  -sublevels in  $^{12}\text{C}_2\text{H}_2$  lower than  $3650 \text{ cm}^{-1}$ .

**Table 1**

$$G_v^0 = \sum_{i=1,5} \tilde{\omega}_i^0 v_i + \sum_{i \leq j} x_{ij}^0 v_i v_j + \sum_{b \leq b'=4,5} x_{l_b l_{b'}}^0 l_b l_{b'} + \sum_{i \leq j \leq m} y_{ijm} v_i v_j v_m + \sum_{i, b \leq b'} y_{i l_b l_{b'}} v_i l_b l_{b'} + \sum_{i \leq j \leq m \leq n} z_{ijmn} v_i v_j v_m v_n + \sum_{i \leq j, b \leq b'} z_{ij l_b l_{b'}} v_i v_j l_b l_{b'} + \sum_{b \leq b' \leq b'' \leq b'''} z_{l_b l_{b'} l_{b''} l_{b'''}} l_b l_{b'} l_{b''} l_{b'''} \quad (1)$$

$$\langle l_4, l_5 | \tilde{H} | l_4 \mp 2, l_5 \pm 2 \rangle = \frac{1}{4} r_{45} \left[ (v_4 \pm l_4)(v_4 \mp l_4 + 2)(v_5 \mp l_5)(v_5 \pm l_5 + 2) \right]^{1/2} \quad (2)$$

$$r_{45} = r_{45}^0 + \sum_i r_{45,i} (v_i - \delta_{i4} - \delta_{i5}) + \sum_{i \leq j} r_{45,ij} (v_i - \delta_{i4} - \delta_{i5})(v_j - \delta_{j4} - \delta_{j5}) + \sum_{b \leq b'} r_{45 l_b l_{b'}} (l_b \pm 1)(l_{b'} \pm 1) + r_{45J} J(J+1) \quad (3)$$

$$r_{45J} = r_{45J}^0 + \sum_i r_{45J,i} (v_i - \delta_{i4} - \delta_{i5}) \quad (4)$$

$$E_{rv}^0 = G_v^0 + B_v [J(J+1) - k^2] - D_v [J(J+1) - k^2]^2 + H_v [J(J+1) - k^2]^3 \quad (5)$$

$$B_v = B_0 - \sum_i \alpha_i^0 v_i + \sum_{i \leq i'} \gamma_{ii'}^0 v_i v_{i'} + \sum_{b \leq b'} \gamma_{l_b l_{b'}}^0 l_b l_{b'} + \sum_{i \leq i' \leq i''} \varepsilon_{ii'i''} v_i v_{i'} v_{i''} + \sum_{i, b \leq b'} \varepsilon_{i l_b l_{b'}} v_i l_b l_{b'} \quad (6)$$

$$D_v = D_0 + \sum_i \beta_i^0 v_i + \sum_{i \leq i'} \beta_{ii'} v_i v_{i'} + \sum_{b \leq b'} \beta_{l_b l_{b'}} l_b l_{b'} \quad (7)$$

$$H_v = H_0 \quad (8)$$

$$\langle l_b | H | l_b \pm 2 \rangle = \frac{1}{4} q_b \left[ (v_b \mp l_b)(v_b \pm l_b + 2) \right]^{1/2} F_{\pm}(J, k) F_{\pm}(J, k \pm 1) \quad (9)$$

$$q_b = q_b^0 + \sum_i q_{bi} (v_i - \delta_{ib}) + q_{bJ} J(J+1) \quad (10)$$

$$q_{bJ} = q_{bJ}^0 + \sum_i q_{bJ,i} (v_i - \delta_{ib}) \quad (11)$$

$$\langle l_b, l_{b'} | H | l_b \pm 4, l_{b'} \mp 2 \rangle = \frac{1}{8} q_{bb'b'} \left[ (v_b \mp l_b)(v_b \pm l_b + 2)(v_b \mp l_b - 2)(v_b \pm l_b + 4)(v_{b'} \pm l_{b'})(v_{b'} \mp l_{b'} + 2) \right]^{1/2} F_{\pm}(J, k) F_{\pm}(J, k \pm 1) \quad (12)$$

$$\langle l_b | H | l_b \pm 4 \rangle = \frac{1}{4} u_{bb} \left[ (v_b \mp l_b)(v_b \pm l_b + 2)(v_b \mp l_b - 2)(v_b \pm l_b + 4) \right]^{1/2} F_{\pm}(J, k) F_{\pm}(J, k \pm 1) F_{\pm}(J, k \pm 2) F_{\pm}(J, k \pm 3) \quad (13)$$

$$\langle l_b l_{b'} | H | l_b \pm 2, l_{b'} \pm 2 \rangle = \frac{1}{4} u_{bb'} [(v_b \mp l_b)(v_b \pm l_b + 2)(v_{b'} \mp l_{b'})(v_{b'} \pm l_{b'} + 2)]^{1/2} F_{\pm}(J, k) F_{\pm}(J, k \pm 1) F_{\pm}(J, k \pm 2) F_{\pm}(J, k \pm 3) \quad (14)$$

$$F_{\pm}(J, k) = [J(J+1) - k(k \pm 1)]^{1/2} \quad (15)$$

$$\langle v_4, v_5, l_4, l_5 | \tilde{H} | v_4 + 2, v_5 - 2, l_4, l_5 \rangle = \frac{1}{4} K_{44/55} [(v_4 - l_4 + 2)(v_4 + l_4 + 2)(v_5 + l_5)(v_5 - l_5)]^{1/2} \quad (16)$$

$$K_{44/55} = K_{44/55}^0 + \sum_i K_{44/55,i} (v_i - 2\delta_{i5}) + K_{44/55,J} [J(J+1) - k^2] \quad (17)$$

$$\langle v_4, v_5, l_4, l_5 | \tilde{H} | v_4 + 2, v_5 - 2, l_4 \pm 2, l_5 \mp 2 \rangle = \frac{1}{8} K'_{44/55} [(v_4 \pm l_4 + 2)(v_4 \pm l_4 + 4)(v_5 \pm l_5)(v_5 \pm l_5 - 2)]^{1/2} \quad (18)$$

$$K'_{44/55} = K_{44/55}^0 + \sum_i K'_{44/55,i} (v_i - 2\delta_{i5}) + K'_{44/55,J} [J(J+1) - k^2] \quad (19)$$

<sup>a</sup> In the terms,  $i, j, m, n$  refer to the five modes of vibration,  $b$  and  $b'$  specifically to the bending ones and  $k = l_4 + l_5$ .

The notation  $\delta_{ij}$  is the usual notation for the delta of Kronecker function.

Table 2

| Transition                         | Symmetry                         | $\nu_C^a$         | Assigned Transitions   |
|------------------------------------|----------------------------------|-------------------|--|
| $2\nu_4 \leftarrow \nu_5$          | $\Sigma_g^+ \leftarrow \Pi_u$    | 501.2361 <i>b</i> | P <sub>e-e</sub> (1-32); R <sub>e-e</sub> (1-29); Q <sub>e-f</sub> (1-31)  |
|                                    | $\Delta_g \leftarrow \Pi_u$      | 499.6459 <i>b</i> | P <sub>e-e</sub> (3-11); R <sub>e-e</sub> (1-12); Q <sub>e-f</sub> (2-37)<br>P <sub>f-f</sub> (3-29); R <sub>f-f</sub> (1-31); Q <sub>f-e</sub> (2-24) |
| $3\nu_4 \leftarrow \nu_4 + \nu_5$  | $\Pi_g \leftarrow \Sigma_u^+$    | 526.5234          | P <sub>e-e</sub> (4-22); R <sub>e-e</sub> (1-21); Q <sub>f-e</sub> (1-22)  |
|                                    | $\Pi_g \leftarrow \Sigma_u^-$    | 514.0461 <i>b</i> | P <sub>f-f</sub> (2-27); R <sub>f-f</sub> (0-24); Q <sub>e-f</sub> (1-26)  |
|                                    | $\Pi_g \leftarrow \Delta_u$      | 511.7947 <i>b</i> | P <sub>e-e</sub> (2-26); R <sub>e-e</sub> (2-28); Q <sub>e-f</sub> (2-18)<br>P <sub>f-f</sub> (2-27); R <sub>f-f</sub> (3-25); Q <sub>f-e</sub> (2-18) |
|                                    | $\Phi_g \leftarrow \Delta_u$     | 508.5698 <i>b</i> | P <sub>e-e</sub> (5-14); R <sub>e-e</sub> (2-19); Q <sub>e-f</sub> (6-29)<br>P <sub>f-f</sub> (5-17); R <sub>f-f</sub> (2-21); Q <sub>f-e</sub> (7-30) |
| $2\nu_4 + \nu_5 \leftarrow 2\nu_5$ | $\Pi\Pi_u \leftarrow \Sigma_g^+$ | 490.8876          | Q <sub>f-e</sub> (3-13)  |
|                                    | $\Pi\Pi_u \leftarrow \Delta_g$   | 481.7063          | P <sub>e-e</sub> (2-15); R <sub>e-e</sub> (3-13); Q <sub>e-f</sub> (2-15)<br>P <sub>f-f</sub> (2-14); R <sub>f-f</sub> (3-14); Q <sub>f-e</sub> (2-19) |
|                                    | $I\Pi_u \leftarrow \Sigma_g^+$   | 510.5802          | P <sub>e-e</sub> (2-25); R <sub>e-e</sub> (0-23); Q <sub>f-e</sub> (1-22)  |
|                                    | $I\Pi_u \leftarrow \Delta_g$     | 501.3989          | P <sub>e-e</sub> (2-18); R <sub>e-e</sub> (2-17); Q <sub>e-f</sub> (2-26)<br>P <sub>f-f</sub> (2-20); R <sub>f-f</sub> (4-19); Q <sub>f-e</sub> (2-23) |
|                                    | $\Phi_u \leftarrow \Delta_g$     | 503.6382          | P <sub>e-e</sub> (4-23); R <sub>e-e</sub> (2-25); Q <sub>e-f</sub> (3-20)<br>P <sub>f-f</sub> (5-22); R <sub>f-f</sub> (2-26); Q <sub>f-e</sub> (3-12) |

<sup>a</sup> The band center (in cm<sup>-1</sup>) is  $\nu_C = G_v^0 - B_v k'^2 - D_v k'^4 - (G_{v''}^0 - B_{v''} k''^2 - D_{v''} k''^4)$

<sup>b</sup> Band previously observed in Ref. (26). The range of the *J* values has been extended.

Table 3

| Upper state<br>$v_4, v_5, l_4, l_5, e/f$ | Lower state<br>$v_4, v_5, l_4, l_5, e/f$ | Lines | Jmax | Ref. |
|--|--|-------|------|------|
| 0 1, 0 1e                                | 0 0, 0 0e                                | 76    | 40   | a    |
| 0 1, 0 1e                                | 1 0, 1 0e                                | 54    | 31   | a    |
| 0 1, 0 1e                                | 1 0, 1 0f                                | 10    | 10   | a    |
| 0 1, 0 1f                                | 1 0, 1 0e                                | 9     | 11   | a    |
| 0 1, 0 1f                                | 1 0, 1 0f                                | 56    | 31   | a    |
| 0 1, 0 1f                                | 0 0, 0 0e                                | 40    | 41   | a    |
| 2 0, 0 0e                                | 0 1, 0 1e                                | 61    | 31   | b    |
| 2 0, 0 0e                                | 0 1, 0 1f                                | 30    | 31   | b    |
| 2 0, 2 0e                                | 0 1, 0 1e                                | 21    | 13   | b    |
| 2 0, 2 0e                                | 0 1, 0 1f                                | 35    | 37   | b    |
| 2 0, 2 0f                                | 0 1, 0 1f                                | 57    | 32   | b    |
| 2 0, 2 0f                                | 0 1, 0 1e                                | 23    | 24   | b    |
| 1 1, 1-1e                                | 1 0, 1 0e                                | 61    | 32   | a    |
| 1 1, 1-1e                                | 1 0, 1 0f                                | 25    | 32   | a    |
| 1 1, 1-1e                                | 2 0, 0 0e                                | 36    | 22   | a    |
| 1 1, 1-1e                                | 0 0, 0 0e                                | 84    | 42   | a    |
| 1 1, 1-1f                                | 1 0, 1 0f                                | 54    | 29   | a    |
| 1 1, 1-1f                                | 1 0, 1 0e                                | 29    | 31   | a    |
| 1 1, 1 1e                                | 1 0, 1 0e                                | 50    | 28   | a    |
| 1 1, 1 1e                                | 1 0, 1 0f                                | 28    | 34   | a    |
| 1 1, 1 1e                                | 2 0, 2 0e                                | 35    | 22   | a    |
| 1 1, 1 1e                                | 0 0, 0 0e                                | 62    | 40   | a    |
| 1 1, 1 1f                                | 1 0, 1 0f                                | 54    | 29   | a    |
| 1 1, 1 1f                                | 1 0, 1 0e                                | 29    | 31   | a    |
| 1 1, 1 1f                                | 2 0, 2 0f                                | 38    | 25   | a    |
| 0 2, 0 0e                                | 0 1, 0 1e                                | 59    | 31   | a    |
| 0 2, 0 0e                                | 0 1, 0 1f                                | 23    | 29   | a    |
| 0 2, 0 0e                                | 1 1, 1-1e                                | 34    | 21   | a    |
| 0 2, 0 2e                                | 0 1, 0 1e                                | 50    | 27   | a    |
| 0 2, 0 2e                                | 0 1, 0 1f                                | 28    | 34   | a    |
| 0 2, 0 2e                                | 1 1, 1 1e                                | 28    | 21   | a    |
| 0 2, 0 2f                                | 0 1, 0 1f                                | 54    | 30   | a    |
| 0 2, 0 2f                                | 1 1, 1 1f                                | 27    | 20   | a    |
| 0 2, 0 2f                                | 0 1, 0 1e                                | 26    | 32   | a    |
| 3 0, 1 0e                                | 1 1, 1-1f                                | 26    | 26   | b    |
| 3 0, 1 0e                                | 1 1, 1-1e                                | 36    | 22   | b    |
| 3 0, 1 0e                                | 1 1, 1 1e                                | 52    | 29   | b    |
| 3 0, 1 0e                                | 1 1, 1 1f                                | 16    | 18   | b    |
| 3 0, 1 0f                                | 1 1, 1-1f                                | 50    | 26   | b    |
| 3 0, 1 0f                                | 1 1, 1-1e                                | 21    | 22   | b    |
| 3 0, 1 0f                                | 1 1, 1 1e                                | 16    | 18   | b    |
| 3 0, 1 0f                                | 1 1, 1 1f                                | 49    | 26   | b    |
| 3 0, 3 0e                                | 1 1, 1 1e                                | 28    | 22   | b    |
| 3 0, 3 0e                                | 1 1, 1 1f                                | 24    | 29   | b    |
| 3 0, 3 0f                                | 1 1, 1 1e                                | 23    | 30   | b    |
| 3 0, 3 0f                                | 1 1, 1 1f                                | 33    | 22   | b    |
| 2 1, 2-1e                                | 2 0, 2 0e                                | 14    | 20   | a    |
| 2 1, 2-1e                                | 1 0, 1 0e                                | 75    | 38   | a    |
| 2 1, 2-1e                                | 2 0, 2 0f                                | 10    | 20   | a    |
| 2 1, 2-1e                                | 0 2, 0 2e                                | 16    | 14   | b    |
| 2 1, 2-1e                                | 0 2, 0 2f                                | 13    | 15   | b    |
| 2 1, 2-1f                                | 0 2, 0 0e                                | 8     | 13   | b    |
| 2 1, 2-1f                                | 1 0, 1 0f                                | 73    | 37   | a    |
| 2 1, 2-1f                                | 0 2, 0 2e                                | 18    | 19   | b    |
| 2 1, 2-1f                                | 0 2, 0 2f                                | 23    | 15   | b    |
| 2 1, 2-1f                                | 2 0, 0 0e                                | 13    | 19   | a    |



|    |            |           |    |    |   |
|----|------------|-----------|----|----|---|
| 1  | 2 1, 2-1f  | 2 0, 2 0e | 8  | 17 | a |
| 2  | 2 1, 2-1f  | 2 0, 2 0f | 10 | 21 | a |
| 3  | 2 1, 0 1e  | 2 0, 0 0e | 24 | 18 | a |
| 4  | 2 1, 0 1e  | 2 0, 2 0f | 4  | 16 | a |
| 5  | 2 1, 0 1e  | 1 0, 1 0e | 23 | 16 | a |
| 6  | 2 1, 0 1e  | 0 2, 0 0e | 48 | 24 | b |
| 7  | 2 1, 0 1e  | 0 2, 0 2e | 33 | 18 | b |
| 8  | 2 1, 0 1e  | 0 2, 0 2f | 24 | 26 | b |
| 9  | 2 1, 0 1f  | 1 0, 1 0f | 43 | 27 | a |
| 10 | 2 1, 0 1f  | 0 2, 0 0e | 22 | 22 | b |
| 11 | 2 1, 0 1f  | 0 2, 0 2f | 29 | 19 | b |
| 12 | 2 1, 0 1f  | 0 2, 0 2e | 19 | 23 | b |
| 13 | 2 1, 2 1e  | 2 0, 2 0e | 12 | 16 | a |
| 14 | 2 1, 2 1e  | 2 0, 2 0f | 8  | 20 | a |
| 15 | 2 1, 2 1e  | 0 2, 0 2e | 44 | 26 | b |
| 16 | 2 1, 2 1e  | 0 2, 0 2f | 15 | 20 | b |
| 17 | 2 1, 2 1f  | 0 2, 0 2f | 43 | 27 | b |
| 18 | 2 1, 2 1f  | 1 0, 1 0f | 28 | 29 | a |
| 19 | 2 1, 2 1f  | 2 0, 2 0e | 7  | 15 | a |
| 20 | 2 1, 2 1f  | 2 0, 2 0f | 17 | 17 | a |
| 21 | 2 1, 0 1e  | 0 2, 0 2e | 10 | 12 | b |
| 22 | 2 1, 0 1f  | 0 0, 0 0e | 22 | 26 | c |
| 23 | 2 1, 0 1f  | 0 0, 0 0e | 9  | 18 | c |
| 24 | 2 1, 2-1e  | 0 0, 0 0e | 41 | 33 | c |
| 25 | 2 1, 2-1f  | 0 0, 0 0e | 19 | 21 | c |
| 26 | 1 2, 1 0e  | 1 1, 1-1e | 23 | 21 | a |
| 27 | 1 2, 1 0e  | 0 1, 0 1e | 65 | 37 | a |
| 28 | 1 2, 1 0f  | 1 1, 1-1e | 18 | 24 | a |
| 29 | 1 2, 1 0f  | 0 1, 0 1f | 71 | 38 | a |
| 30 | 1 2, -1 2e | 0 1, 0 1e | 49 | 29 | a |
| 31 | 1 2, -1 2e | 1 1, 1-1f | 20 | 23 | a |
| 32 | 1 2, -1 2f | 1 1, 1-1f | 22 | 20 | a |
| 33 | 1 2, -1 2f | 0 1, 0 1f | 48 | 28 | a |
| 34 | 1 2, 1 2e  | 1 1, 1 1e | 17 | 19 | a |
| 35 | 1 2, 1 2e  | 1 1, 1 1f | 12 | 23 | a |
| 36 | 1 2, 1 2f  | 1 1, 1 1e | 12 | 18 | a |
| 37 | 1 2, 1 2f  | 1 1, 1 1f | 15 | 20 | a |
| 38 | 0 3, 0 1e  | 0 2, 0 0e | 24 | 20 | a |
| 39 | 0 3, 0 1e  | 0 2, 0 2e | 1  | 8  | a |
| 40 | 0 3, 0 1e  | 0 2, 0 2f | 2  | 12 | a |
| 41 | 0 3, 0 1f  | 0 2, 0 0e | 17 | 21 | a |
| 42 | 0 3, 0 1f  | 0 2, 0 2e | 5  | 17 | a |
| 43 | 0 3, 0 1f  | 0 2, 0 2f | 1  | 7  | a |
| 44 | 0 3, 0 3e  | 0 2, 0 2e | 14 | 22 | a |
| 45 | 0 3, 0 3f  | 0 2, 0 2f | 15 | 21 | a |
| 46 | 0 3, 0 1e  | 0 0, 0 0e | 45 | 36 | c |
| 47 | 0 3, 0 1f  | 0 0, 0 0e | 16 | 35 | c |
| 48 | 3 1, 1-1e  | 2 0, 0 0e | 59 | 30 | a |
| 49 | 3 1, 3-1e  | 2 0, 2 0e | 37 | 32 | a |
| 50 | 3 1, 3-1f  | 2 0, 2 0f | 37 | 31 | a |
| 51 | 3 1, 3-1e  | 1 0, 1 0e | 19 | 26 | c |
| 52 | 3 1, 3-1f  | 1 0, 1 0f | 17 | 25 | c |
| 53 | 3 1, 1 1e  | 1 0, 1 0e | 2  | 11 | c |
| 54 | 3 1, 1 1f  | 1 0, 1 0f | 3  | 12 | c |
| 55 | 2 2, 2-2e  | 1 1, 1-1e | 59 | 31 | a |
| 56 | 2 2, 2-2f  | 1 1, 1-1f | 38 | 24 | a |
| 57 | 2 2, 2-2f  | 1 1, 1 1f | 14 | 24 | a |
| 58 | 2 2, 2 0e  | 1 1, 1 1e | 42 | 29 | a |
| 59 | 2 2, 2 0f  | 1 1, 1 1f | 40 | 28 | a |
| 60 | 2 2, 2 0f  | 1 1, 1-1f | 28 | 27 | a |
|    | 2 2, 2-2e  | 0 1, 0 1e | 8  | 19 | c |
|    | 2 2, 2-2e  | 0 1, 0 1f | 7  | 21 | c |
|    | 2 2, 2-2f  | 0 1, 0 1f | 1  | 8  | c |

|    |            |           |    |    |   |
|----|------------|-----------|----|----|---|
| 1  | 2 2, 2 0f  | 0 1, 0 1f | 3  | 22 | c |
| 2  | 1 3, 1-1e  | 0 2, 0 0e | 37 | 26 | a |
| 3  | 1 3, 1 1e  | 0 2, 0 2e | 46 | 26 | a |
| 4  | 1 3, 1 1f  | 0 2, 0 2f | 44 | 27 | a |
| 5  | 1 3, 1-1e  | 1 0, 1 0e | 19 | 21 | c |
| 6  | 1 3, 1-1e  | 1 0, 1 0f | 16 | 18 | c |
| 7  | 1 3, 1-1f  | 1 0, 1 0f | 28 | 25 | c |
| 8  | 1 3, 1-1f  | 1 0, 1 0e | 13 | 22 | c |
| 9  | 1 3, 1 1e  | 1 0, 1 0e | 14 | 22 | c |
| 10 | 1 3, 1 1f  | 1 0, 1 0e | 13 | 21 | c |
| 11 | 1 3, 1 1f  | 1 0, 1 0f | 16 | 22 | c |
| 12 | 1 3, 1 1e  | 1 0, 1 0f | 13 | 19 | c |
| 13 | 1 3, -1 3e | 1 0, 1 0e | 15 | 16 | c |
| 14 | 1 3, -1 3f | 1 0, 1 0e | 18 | 24 | c |
| 15 | 1 3, -1 3f | 1 0, 1 0f | 14 | 18 | c |
| 16 | 1 3, -1 3e | 1 0, 1 0f | 20 | 27 | c |
| 17 | 0 4, 0 0e  | 0 1, 0 1e | 28 | 28 | c |
| 18 | 0 4, 0 0e  | 0 1, 0 1f | 7  | 24 | c |
| 19 | 0 4, 0 2e  | 0 1, 0 1e | 21 | 22 | c |
| 20 | 0 4, 0 2f  | 0 1, 0 1e | 13 | 26 | c |
| 21 | 0 4, 0 2f  | 0 1, 0 1f | 27 | 25 | c |
| 22 | 0 4, 0 2e  | 0 1, 0 1f | 15 | 26 | c |

| Upper state                        | Lower state                        | Lines | Jmax | Ref. |
|------------------------------------|------------------------------------|-------|------|------|
| $v_1 v_2 v_3 v_4 v_5, l_4 l_5 e/f$ | $v_1 v_2 v_3 v_4 v_5, l_4 l_5 e/f$ |       |      |      |
| 0 1 0 0 0, 0 0e                    | 0 0 0 0 1, 0 1e                    | 44    | 25   | a    |
| 0 1 0 0 0, 0 0e                    | 0 0 0 0 1, 0 1f                    | 27    | 27   | a    |
| 0 1 0 1 0, 1 0e                    | 0 0 0 0 1, 0 1e                    | 26    | 19   | c    |
| 0 1 0 1 0, 1 0f                    | 0 0 0 0 1, 0 1f                    | 26    | 22   | c    |
| 0 1 0 0 1, 0 1e                    | 0 0 0 1 0, 1 0e                    | 24    | 20   | c    |
| 0 1 0 0 1, 0 1f                    | 0 0 0 1 0, 1 0f                    | 26    | 20   | c    |

† All labels are identified in the text. Ref. a is Kabbadj et al (26);  
Ref. b is the present work; Ref. c is Jacquemart et al. (53).

**Table 4**

|    |         |                |      |
|----|---------|----------------|------|
| 1  |         |                |      |
| 2  |         |                |      |
| 3  |         |                |      |
| 4  | v2      | 1974.31608 (6) |      |
| 5  | omega4  | 608.99047 (41) |      |
| 6  | omega5  | 729.17192 (26) |      |
| 7  | x24     | -12.48073 (7)  |      |
| 8  | x25     | -1.56679 (8)   |      |
| 9  | x44     | 3.15781 (44)   |      |
| 10 | x45     | -2.41149 (32)  |      |
| 11 | x55     | -2.42536 (17)  |      |
| 12 | x1414   | 0.71311 (20)   |      |
| 13 | x1415   | 6.51660 (33)   |      |
| 14 | x1515   | 3.58436 (21)   |      |
| 15 | y444    | 0.01726 (10)   |      |
| 16 | y445    | 0.08842 (43)   |      |
| 17 | y455    | 0.05181 (18)   |      |
| 18 | y555    | 0.01646 (10)   |      |
| 19 | y41414  | -0.00689 (11)  |      |
| 20 | y41415  | 0.03648 (49)   |      |
| 21 | y41515  | 0.00671 (61)   |      |
| 22 | y51414  | -0.03180 (50)  |      |
| 23 | y51415  | 0.05375 (32)   |      |
| 24 | y51515  | -0.01309 (11)  |      |
| 25 | z4445   | -0.00766 (11)  |      |
| 26 | z5555   | -0.00134 (2)   |      |
| 27 | z451414 | 0.00898 (18)   |      |
| 28 | z551414 | 0.00719 (20)   |      |
| 29 | z14555  | -0.00209 (5)   |      |
| 30 | B0      | 1176.64618 (1) | E-03 |
| 31 | alpha2  | 6.18058 (21)   | E-03 |
| 32 | alpha4  | -1.35493 (16)  | E-03 |
| 33 | alpha5  | -2.22742 (14)  | E-03 |
| 34 | gam24   | -7.238 (33)    | E-05 |
| 35 | gam25   | -5.814 (34)    | E-05 |
| 36 | gam44   | -0.159 (14)    | E-05 |
| 37 | gam45   | -2.079 (14)    | E-05 |
| 38 | gam55   | 2.175 (15)     | E-05 |
| 39 | g1414   | -6.568 (16)    | E-05 |
| 40 | g1415   | -22.276 (14)   | E-05 |
| 41 | g1515   | -10.675 (14)   | E-05 |
| 42 | eps444  | 0.0177 (34)    | E-05 |
| 43 | eps445  | 0.327 (15)     | E-05 |
| 44 | eps455  | -0.398 (14)    | E-05 |
| 45 | eps4144 | 0.0505 (58)    | E-05 |
| 46 | eps4145 | 0.207 (10)     | E-05 |
| 47 | eps4155 | 0.252 (11)     | E-05 |
| 48 | eps5144 | -0.483 (12)    | E-05 |
| 49 | eps5145 | -0.566 (12)    | E-05 |
| 50 | eps5155 | -0.1675 (41)   | E-05 |
| 51 | D0      | 1.62655 (1)    | E-06 |
| 52 | beta4   | 3.2289 (58)    | E-08 |
| 53 | beta5   | 2.4434 (43)    | E-08 |
| 54 | H0      | 1.264 (70)     | E-12 |
| 55 | q4      | -5.23080 (10)  | E-03 |
| 56 | q4v2    | -0.02371 (35)  | E-03 |
| 57 | q4v4    | 0.01097 (6)    | E-03 |
| 58 | q4v5    | -0.08183 (20)  | E-03 |
| 59 | q4J     | 3.931 (12)     | E-08 |
| 60 | q4Jv5   | 0.236 (15)     | E-08 |
|    | q5      | -4.69849 (8)   | E-03 |

|    |          |               |      |
|----|----------|---------------|------|
| 1  | q5v2     | 0.00315 (34)  | E-03 |
| 2  | q5v4     | -0.11777 (20) | E-03 |
| 3  | q5v5     | -0.04096 (13) | E-03 |
| 4  | q5v55    | -0.1188 (42)  | E-05 |
| 5  | q5J      | 3.8490 (89)   | E-08 |
| 6  | q5Jv4    | 0.315 (16)    | E-08 |
| 7  | q445     | 0.464 (11)    | E-05 |
| 8  | q455     | 0.472 (11)    | E-05 |
| 9  | u44      | -0.0578 (35)  | E-08 |
| 10 | u45      | -0.5666 (75)  | E-08 |
| 11 | u55      | -0.1130 (24)  | E-08 |
| 12 | r45      | -6.23884 (2)  |      |
| 13 | r45v4    | 0.0637 (13)   |      |
| 14 | r45v5    | -0.0215 (18)  |      |
| 15 | r45v45   | -6.455 (59)   | E-02 |
| 16 | r45v55   | 2.965 (33)    | E-02 |
| 17 | r45l45   | -2.220 (24)   | E-02 |
| 18 | r45J     | 19.6567 (66)  | E-05 |
| 19 | r45Jv4   | -0.601 (26)   | E-05 |
| 20 | r45Jv5   | 0.923 (26)    | E-05 |
| 21 | k4455    | -8.8647 (47)  |      |
| 22 | k4455v4  | 0.1742 (45)   |      |
| 23 | k4455v5  | 0.2145 (33)   |      |
| 24 | k4455J   | 2.24 (54)     | E-05 |
| 25 | kp4455   | 2.675 (37)    |      |
| 26 | kp4455v5 | 0.8399 (75)   |      |
| 27 | kp4455J  | -5.19 (46)    | E-05 |

<sup>a</sup> The standard deviation ( $1\sigma$ ) is indicated in parentheses, in the units of the last quoted digit. The parameters are labeled in agreement with the model defined in table 1.

Table 5

| $v_1$ | $v_2$ | $v_3$ | $v_4$ | $v_5$ | $l_4$ | $l_5$ | e/f | $k$ | $G_c$ (cm <sup>-1</sup> ) |
|-------|-------|-------|-------|-------|-------|-------|-----|-----|---------------------------|
| 0     | 0     | 0     | 0     | 0,    | 0     | 0     | e   | 0   | 0.00000                   |
| 0     | 0     | 0     | 1     | 0,    | 1     | 0     | *   | 1   | 611.69383                 |
| 0     | 0     | 0     | 0     | 1,    | 0     | 1     | *   | 1   | 729.15416                 |
| 0     | 0     | 0     | 2     | 0,    | 2     | 0     | *   | 2   | 1228.80004                |
| 0     | 0     | 0     | 2     | 0,    | 0     | 0     | e   | 0   | 1230.39040                |
| 0     | 0     | 0     | 1     | 1,    | 1     | -1    | e   | 0   | 1328.07329                |
| 0     | 0     | 0     | 1     | 1,    | 1     | -1    | f   | 0   | 1340.55097                |
| 0     | 0     | 0     | 1     | 1,    | 1     | 1     | *   | 2   | 1342.80227                |
| 0     | 0     | 0     | 0     | 2,    | 0     | 0     | e   | 0   | 1449.11243                |
| 0     | 0     | 0     | 0     | 2,    | 0     | 2     | *   | 2   | 1458.29341                |
| 0     | 0     | 0     | 3     | 0,    | 3     | 0     | *   | 3   | 1851.37377                |
| 0     | 0     | 0     | 3     | 0,    | 1     | 0     | *   | 1   | 1854.59688                |
| 0     | 0     | 0     | 2     | 1,    | 2     | -1    | *   | 1   | 1939.99995                |
| 0     | 0     | 0     | 2     | 1,    | 0     | 1     | *   | 1   | 1959.69224                |
| 0     | 0     | 0     | 2     | 1,    | 2     | 1     | *   | 3   | 1961.93143                |
| 0     | 1     | 0     | 0     | 0,    | 0     | 0     | e   | 0   | 1974.31608                |
| 0     | 0     | 0     | 1     | 2,    | 1     | 0     | *   | 1   | 2047.87635                |
| 0     | 0     | 0     | 1     | 2,    | -1    | 2     | *   | 1   | 2065.79309                |
| 0     | 0     | 0     | 1     | 2,    | 1     | 2     | *   | 3   | 2074.18003                |
| 0     | 0     | 0     | 0     | 3,    | 0     | 1     | *   | 1   | 2169.15712                |
| 0     | 0     | 0     | 0     | 3,    | 0     | 3     | *   | 3   | 2187.45070                |
| 0     | 0     | 0     | 4     | 0,    | 4     | 0     | *   | 4   | 2479.46837                |
| 0     | 0     | 0     | 4     | 0,    | 2     | 0     | *   | 2   | 2484.35832                |
| 0     | 0     | 0     | 4     | 0,    | 0     | 0     | e   | 0   | 2485.98868                |
| 0     | 0     | 0     | 3     | 1,    | 3     | -1    | *   | 2   | 2556.79471                |
| 0     | 0     | 0     | 3     | 1,    | 1     | -1    | e   | 0   | 2560.59507                |
| 0     | 1     | 0     | 1     | 0,    | 1     | 0     | *   | 1   | 2573.53543                |
| 0     | 0     | 0     | 3     | 1,    | 1     | -1    | f   | 0   | 2583.84207                |
| 0     | 0     | 0     | 3     | 1,    | 1     | 1     | *   | 2   | 2584.96190                |
| 0     | 0     | 0     | 3     | 1,    | 3     | 1     | *   | 4   | 2586.59122                |
| 0     | 0     | 0     | 2     | 2,    | 2     | -2    | e   | 0   | 2648.01462                |
| 0     | 0     | 0     | 2     | 2,    | 2     | -2    | f   | 0   | 2661.18948                |
| 0     | 0     | 0     | 2     | 2,    | 2     | 0     | *   | 2   | 2661.42934                |
| 0     | 0     | 0     | 2     | 2,    | 0     | 0     | e   | 0   | 2684.00463                |
| 0     | 0     | 0     | 2     | 2,    | 0     | 2     | *   | 2   | 2687.80532                |
| 0     | 0     | 0     | 2     | 2,    | 2     | 2     | *   | 4   | 2695.46775                |
| 0     | 1     | 0     | 0     | 1,    | 0     | 1     | *   | 1   | 2701.90968                |
| 0     | 0     | 0     | 1     | 3,    | 1     | -1    | e   | 0   | 2757.79806                |
| 0     | 0     | 0     | 1     | 3,    | 1     | 1     | *   | 2   | 2768.45002                |
| 0     | 0     | 0     | 1     | 3,    | 1     | -1    | f   | 0   | 2783.65014                |
| 0     | 0     | 0     | 1     | 3,    | -1    | 3     | *   | 2   | 2790.76353                |
| 0     | 0     | 0     | 1     | 3,    | 1     | 3     | *   | 4   | 2805.99802                |
| 0     | 0     | 0     | 0     | 4,    | 0     | 0     | e   | 0   | 2880.22061                |
| 0     | 0     | 0     | 0     | 4,    | 0     | 2     | *   | 2   | 2889.32359                |
| 0     | 0     | 0     | 0     | 4,    | 0     | 4     | *   | 4   | 2916.67339                |
| 0     | 0     | 0     | 5     | 0,    | 5     | 0     | *   | 5   | 3113.14013                |
| 0     | 0     | 0     | 5     | 0,    | 3     | 0     | *   | 3   | 3119.72139                |
| 0     | 0     | 0     | 5     | 0,    | 1     | 0     | *   | 1   | 3123.00307                |
| 0     | 0     | 0     | 4     | 1,    | 4     | -1    | *   | 3   | 3178.94442                |
| 0     | 0     | 0     | 4     | 1,    | 2     | -1    | *   | 1   | 3185.54077                |
| 0     | 0     | 0     | 4     | 1,    | 0     | 1     | *   | 1   | 3214.64385                |
| 0     | 0     | 0     | 4     | 1,    | 2     | 1     | *   | 3   | 3215.97025                |
| 0     | 0     | 0     | 4     | 1,    | 4     | 1     | *   | 5   | 3216.82087                |
| 0     | 0     | 0     | 3     | 2,    | 3     | -2    | *   | 1   | 3260.63757                |
| 0     | 0     | 0     | 3     | 2,    | 3     | 0     | *   | 3   | 3280.51717                |





Figure 2

