

Analysis and fit of the Fourier-transform microwave spectrum of the two-top molecule *N*-methylacetamide

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Abstract

The jet-cooled Fourier-transform microwave spectrum of *N*-methylacetamide ($\text{CH}_3\text{—NH—C(=O)—CH}_3$), a molecule containing two methyl tops with relatively low barriers to internal rotation, has been recorded and fit to nearly experimental uncertainty. Measurements were carried out between 10 and 26 GHz, with the nitrogen quadrupole splittings resolved for many transitions. The permutation-inversion group for this molecule is G_{18} (not isomorphic to any point group), with irreducible representations A_1 , A_2 , E_1 , E_2 , E_3 , and E_4 . One of these symmetry species and the usual three asymmetric rotor quantum numbers $J_{K_a K_c}$ were assigned to each torsion–rotation level involved in the observed transitions. F values were assigned to hyperfine components, where $\mathbf{F} = \mathbf{J} + \mathbf{I}_\text{N}$. Transitions involving levels of A_1 and A_2 species could be fit to an asymmetric rotor Hamiltonian. The other transitions were first fit separately for each symmetry species using a Pickett-like effective rotational Hamiltonian. Constants from these fits show a number of additive properties which can be correlated with sums and differences of effects involving the two tops. A final global fit to 48 molecular parameters for 839 hyperfine components of 216 torsion–rotation transitions involving 152 torsion–rotation levels was carried out using a newly written two-top computer program, giving a root-mean-square deviation of observed-minus-calculated residuals of 4 kHz. This program was written in the principal axis system of the molecule and uses a free-rotor basis set for each top, a symmetric-top basis set for the rotational functions, and a single-step diagonalization procedure. Such an approach requires quite long computation times, but it is much less prone to subtle programming errors (a consideration felt to be important since checking the new program against precise fits of low-barrier two-top molecules in the literature was not possible). The two internal rotation angles in this molecule correspond to the Ramachandran angles ψ and ϕ often defined to describe polypeptide folding. Barriers to internal rotation about these two angles were found to be 73 and 79 cm^{-1} , respectively. Top–top coupling in both the kinetic and potential energy part of the Hamiltonian is relatively small in this molecule.

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1. Introduction

N-Methylacetamide, $\text{CH}_3\text{—C(=O)—NH—CH}_3$, is of spectroscopic interest as a two-top molecule with relatively low barriers to internal rotation of the methyl groups. It can also be viewed as a peptide linkage —C(=O)—NH— capped on either end by a methyl

group, so that the two Ramachandran angles ψ and ϕ , whose variation is normally used to adjust the degree of folding in longer polypeptide chains, become in this case simply the angles of internal rotation for each methyl group.

A number of properties for *N*-methylacetamide, including structures, energies, vibrational frequencies, and NMR chemical shifts for both the *trans* and *cis* isomers, have recently been computed using density functional theory [1] and compared with experimental information

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where available. These theoretical results indicate that the lowest energy structure has a planar heavy atom skeleton with the amido H *trans* to the carbonyl O, and that a second, slightly non-planar skeletal structure with the amido H *cis* to the carbonyl O lies about 880 cm^{-1} higher.

Smeyers and co-workers (e.g. [2–5]) have considered the general two-top internal rotor problem for a number of molecules, using: (i) quantum chemistry calculations to determine the complicated multi-top potential energy surface, (ii) group theoretical transformations to treat any symmetry exhibited by the molecular system, and (iii) two-top torsional Hamiltonians to determine torsional energy level patterns. These workers did not treat the torsion–rotation problem, however, so their results must be extended if application to microwave studies of rotational transitions is desired.

No previous microwave studies of *N*-methylacetamide were found in the literature, but a study of its vibrations in the low-temperature solid does exist [6]. A number of microwave studies of other two-methyl-top molecules have been published, however. These can be divided into two groups. The first involves molecules with two identical tops, so that the group theory, torsion–rotation Hamiltonian, and splitting patterns are somewhat different from those treated here. For recent examples of such studies, see [7–16]. For recent examples of the second group, which involves molecules with two inequivalent methyl tops like that studied here, see [17].

2. Experimental

The Fourier-transform microwave (FTMW) spectrum of *N*-methylacetamide (NMA) was measured in the range from 9.9 to 26.5 GHz using one of the mini FTMW spectrometers at NIST. This instrument was equipped with a reservoir nozzle that was heated to around 60°C to increase the sample concentration in the

molecular beam. The carrier gas was an 80%/20% mixture of neon and helium. The nozzle was mounted in the end flange/mirror to give coaxial injection into the microwave cavity. The instrument, automated scanning, and measurement procedures have been described in detail previously [18,19]. All frequency measurements are referenced to a rubidium frequency standard.

In the initial work, large automated survey scans were recorded using 10 nozzle pulses per frequency step. The results from these scans were then imported into NIST's JB95 spectral fitting program for analysis [20–22]. A set of combined scans covering the frequency range of 11.5–26.0 GHz is shown in the upper trace of Fig. 1. Using a standard rigid rotor analysis it was possible to assign a set of transitions that belong to the *AA* state of the molecule (i.e., the state with both rotors in their lowest, and therefore non-degenerate, torsional component). Nuclear quadrupole splittings were readily apparent on most of the transitions, and a hyperfine analysis for the *AA* state was also performed using the JB95 program. The simulated *AA*-state spectrum resulting from this fit (see Section 4) is shown in the lower trace of Fig. 1.

It was apparent from the initial fit of the *AA*-state transitions that many lines remained unassigned in the spectrum. Based on previous studies of acetamide [19] and *N*-methylformamide [23], we expected each methyl top to have a low barrier to internal rotation, giving rise to a total of five internal rotor states (see Section 3), which would then account for the remaining lines in the spectrum.

3. Group theory and qualitative energy level diagram

If one assumes that the four atoms in the peptide linkage and the two methyl carbon atoms all lie in the same plane, as predicted from the *ab initio* study [1], and that both methyl tops exhibit internal rotation motion, then the permutation-inversion group for NMA can be

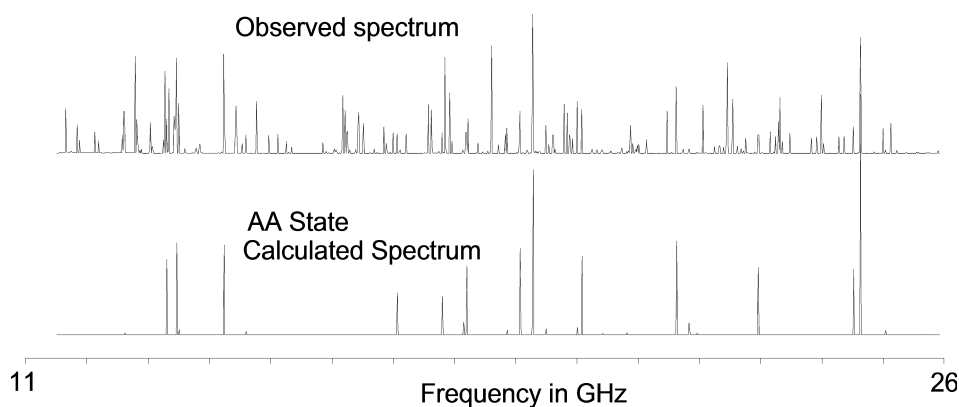


Fig. 1. The composite experimental spectrum from 11.5 to 26.0 GHz (upper trace). Simulated rigid-rotor transitions for the *AA* state (lower trace). Note that there are many more transitions in the experimental spectrum than are accounted for by the *AA* state alone.

denoted by G_{18} , a group with two non-degenerate and four doubly degenerate symmetry species: A_1 , A_2 , E_1 , E_2 , E_3 , and E_4 . The character table for this group was first given by Bunker [24], but it is reproduced here as Table 1 to specify a particular way (see Section 5) of relating the +2 characters of the four E states to the various one-top and two-top internal rotation operations.

There is also potential confusion when using a labeling scheme based on A and E symmetry species for the individual rotors, as can be seen from the two alternatives presented in columns 1 and 2 of Table 3 of [9]. The scheme in column 1 is appropriate when the two methyl tops are equivalent. (See also Tables 6–10 of [25].) Since the two methyl groups in *N*-methylacetamide are inequivalent (corresponding group-theoretically to the $^{32}\text{S}^{34}\text{S}$ isotopomer of dimethyl disulfide discussed in [9]), we adopt here the AA , EA , AE , and EE labeling in column 2, headed $C_3^1 \otimes C_3^2$, where the superscripts indicate top 1 and top 2, respectively. This notation also corresponds closely to the $\sigma_1 \sigma_2$ integer labels for the individual tops given in column 3 of that table. As can be seen from Table 1, the (A_1, A_2) , E_1 , E_2 , and (E_3, E_4) symmetry species in our G_{18} have been chosen to correspond to individual-top AA , EA , AE , and EE labels, respectively. For convenience, we will often use an unsubscripted A to indicate either of the two non-degenerate species A_1 or A_2 , since the A_1 and A_2 labels essentially discriminate only between the two components of a K -type doublet.

A qualitative $J = K = 0$ energy level diagram can be constructed as illustrated by the four columns of levels shown in Fig. 2. The level at the very left represents the situation before any internal rotation interactions have been turned on. The two levels in the next column are the usual A and E components arising in the one-top problem. They are shifted to positions at $-2\Delta_1$ and $+\Delta_1$, respectively (with $\Delta_1 > 0$ for $v=\text{even}$) when internal rotation of top 1 is turned on. Each of these levels is again split into an A and E component, shifted to po-

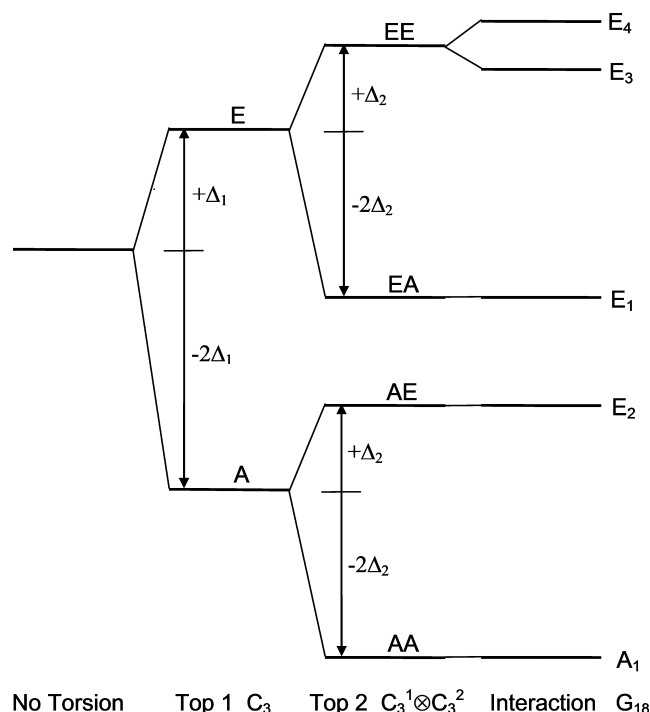


Fig. 2. Schematic $J = K = 0$ torsional energy level diagram for the two-top problem in *N*-methylacetamide. The level at the left is first split into an A and E torsional component by internal rotation tunneling of top 1. Each of these levels is then split again into an A and E torsional component by internal rotation tunneling of top 2. Finally, the apparently fourfold degenerate level at the top is split into two doubly degenerate levels by top–top interaction. The diagram is drawn with $\Delta_1 > \Delta_2 > 0$, using the G_{18} species notation of Table 1, and corresponds to the actual energy level ordering in *N*-methylacetamide.

sitions at $-2\Delta_2$ and $+\Delta_2$, respectively (for $\Delta_2 > 0$) when internal rotation of top 2 is turned on. This gives rise (for $\Delta_1 > \Delta_2 > 0$) to the four-level energy pattern shown in the third column. When the two tops are allowed to interact by some mechanism, the fourfold degenerate EE level at the top of the third column splits into two doubly degenerate levels (since the PI group G_{18} has no fourfold irreducible representations). If the top–top

Table 1
Character table for the group G_{18} appropriate for *N*-methylacetamide

	E	2 (456) ^a	2 (123) ^a	2 (123)(456) ^b	2 (123)(465) ^b	9 (23)(56) ^a	$C_3^1 \otimes C_3^2$	σ_1	σ_2	W^c
A_1	1	1	1	1	1	1	AA	0	0	16
A_2	1	1	1	1	1	−1	AA	0	0	16
E_1	2	2	−1	−1	−1	0	EA	± 1	0	16
E_2	2	−1	2	−1	−1	0	AE	0	± 1	16
E_3	2	−1	−1	2	−1	0	EE	± 1	∓ 1	8
E_4	2	−1	−1	−1	2	0	EE	± 1	± 1	8

^a Top 1 is the N—CH₃ group, with hydrogens 1, 2, and 3. Top 2 is the C—CH₃ group, with hydrogens 4, 5, and 6. The hydrogens are numbered such that (123) and (456) generate angular momenta pointing in the same direction in the molecule. These two columns in the table have been arranged so that $E(\text{top 1}) \otimes A(\text{top 2})$ is of species E_1 and $A(\text{top 1}) \otimes E(\text{top 2})$ is of species E_2 , as indicated in the column headed $C_3^1 \otimes C_3^2$.

^b These two columns have been arranged so that E_3 and E_4 correspond to subtraction and addition of the angular momenta, respectively, when the two tops are in E states rotating at the same speed in the molecule.

^c Statistical weight.

interaction splitting is small, the five-level energy pattern shown in the fourth column is obtained. The physical characteristics of the five levels are as follows: AA has no angular momentum in either top; EA and AE have angular momentum in one top but not in the other; EE has angular momentum in both tops, which can be coupled either in phase or out of phase. Fig. 2 turns out to be a reasonable approximation to the torsional energy level pattern for *N*-methylacetamide, essentially because the two tops are well separated from each other in this molecule, and their mutual interaction is therefore rather small.

4. Line assignments and separate fits for each symmetry species

Assignments of the measured absorption lines were carried out primarily with the help of closed loops of transition frequencies (equivalent to using combination differences) and also by examining separate fits for each of the symmetry species. These separate fits, as described below, were quite helpful for establishing both the J , K_a , K_c assignments and the symmetry species assignments. In toto, 839 hyperfine components of 216 torsion-rotation transitions involving 152 torsion-rotation levels were assigned and fit.

An effective rotational Hamiltonian operator of the following form was used for each of the separate-symmetry fits:

$$H(\Gamma)_{\text{eff-rot}} = AJ_z^2 + BJ_x^2 + CJ_y^2 - \Delta_J \mathbf{J}^4 - \Delta_{JK} \mathbf{J}^2 J_z^2 - \Delta_K J_z^4 \\ - 2\delta_J \mathbf{J}^2 (J_x^2 - J_y^2) - \delta_K [J_z^2 (J_x^2 - J_y^2) \\ + (J_x^2 - J_y^2) J_z^2] + (q + q_J \mathbf{J}^2 + q_K J_z^2 + q_{JK} \mathbf{J}^2 J_z) J_z \\ + (r + r_J \mathbf{J}^2) J_x + (1/2) r_K (J_z^2 J_x + J_x J_z^2), \quad (1)$$

where all the coefficients are real constants for each of the symmetry species $\Gamma = A_1, A_2, E_1, E_2, E_3$, or E_4 .

Note that the terms in odd powers of the angular momentum components J_x , J_y , and J_z occurring in Eq. (1) transform into their negatives, i.e., are not invariant, under the time-reversal operation. This deviation from normal Hamiltonian behavior arises because the coefficients of these terms in the effective rotational Hamiltonian implicitly contain numerical expectation values of an odd power of the torsional angular momentum operators of the two methyl tops. When these p_1 and p_2 torsional operators are included explicitly in the torsion-rotation Hamiltonian (see Eqs. (4)), they also transform into their negatives under time reversal, making the complete Hamiltonian invariant as it should be.

Values for the parameters in Eq. (1) determined from the separate fits are given in Table 2 for each of the symmetry species Γ . As is well known, the q and r terms, which are linear in J_z and J_x , respectively, and which arise from Coriolis interactions between the internal-

rotation angular momentum and the overall-rotation angular momentum, as well as the odd-power centrifugal distortion corrections for these terms, need not be used in the fit for the AA species transitions. This arises because A torsional wavefunctions give zero expectation values for odd powers of the torsional angular momentum operator. As mentioned in Section 2, a preliminary set of AA transitions were first fit in this study using an ordinary asymmetric rotor Hamiltonian, which gave molecular parameters essentially identical to those found in the A -species column of Table 2.

Some parameters in Table 2 can be seen to obey approximate empirical relations of the form:

$$\begin{aligned} q(E_1\text{-species}) - q(E_2\text{-species}) &\approx q(E_3\text{-species}), \\ q(E_1\text{-species}) + q(E_2\text{-species}) &\approx q(E_4\text{-species}), \\ r(E_1\text{-species}) - r(E_2\text{-species}) &\approx r(E_3\text{-species}), \\ r(E_1\text{-species}) + r(E_2\text{-species}) &\approx r(E_4\text{-species}) \end{aligned} \quad (2)$$

and

$$\begin{aligned} [A(A\text{-species}) - A(E_1\text{-species})] \\ + [A(A\text{-species}) - A(E_2\text{-species})] \\ \approx [A(A\text{-species}) - A(E_3\text{-species})] \\ \approx [A(A\text{-species}) - A(E_4\text{-species})]. \end{aligned} \quad (3)$$

Relations like Eqs. (2), which are also obeyed by the centrifugal distortion correction terms for q and r , arise naturally if there is relatively little interaction between the two methyl tops, so that the two-top torsional wavefunctions are well approximated by binary products of one-top A and E functions chosen from within a fixed set for top 1 and top 2. One can then write, for example,

$$\begin{aligned} q(E_1)J_z &= q(E_+A)J_z \\ &= \langle \psi_{1E+} \psi_{2A} | aJ_z p_1 + bJ_z p_2 | \psi_{1E+} \psi_{2A} \rangle \\ &= a \langle \psi_{1E+} | p_1 | \psi_{1E+} \rangle J_z, \\ q(E_2)J_z &= q(AE_+)J_z \\ &= \langle \psi_{1A} \psi_{2E+} | aJ_z p_1 + bJ_z p_2 | \psi_{1A} \psi_{2E+} \rangle \\ &= b \langle \psi_{2E+} | p_2 | \psi_{2E+} \rangle J_z, \\ q(E_3)J_z &= q(E_+E_-)J_z \\ &= \langle \psi_{1E+} \psi_{2E-} | aJ_z p_1 + bJ_z p_2 | \psi_{1E+} \psi_{2E-} \rangle \\ &= [a \langle \psi_{1E+} | p_1 | \psi_{1E+} \rangle - b \langle \psi_{2E+} | p_2 | \psi_{2E+} \rangle] J_z \\ &= [q(E_1) - q(E_2)] J_z, \\ q(E_4)J_z &= q(E_+E_+)J_z \\ &= \langle \psi_{1E+} \psi_{2E+} | aJ_z p_1 + bJ_z p_2 | \psi_{1E+} \psi_{2E+} \rangle \\ &= [a \langle \psi_{1E+} | p_1 | \psi_{1E+} \rangle + b \langle \psi_{2E+} | p_2 | \psi_{2E+} \rangle] J_z \\ &= [q(E_1) + q(E_2)] J_z. \end{aligned} \quad (4)$$

Eqs. (4) and the good numerical agreement between values for the left and right sides of Eqs. (2) from Table 2 indicate that the doubly degenerate symmetry species E_1 , E_2 , and (E_3, E_4) here correspond well to EA , AE , and EE in the traditional usage, respectively. Note that the relations between the q 's derived in Eqs. (4) do not depend

Table 2

Molecular parameters^a (MHz) of *N*-methylacetamide obtained from separate fits for each symmetry species

	<i>A</i>	<i>E</i> ₁	<i>E</i> ₂	<i>E</i> ₃	<i>E</i> ₄
<i>A</i>	10558.92531(74)	10199.0086(22)	10206.6385(20)	9889.5958(18)	9857.7697(24)
<i>B</i>	3898.44610(20)	3889.84640(28)	3884.92129(65)	3876.19706(30)	3875.8339(14)
<i>C</i>	2904.99737(17)	2906.27220(23)	2905.13578(51)	2906.79731(25)	2905.9374(13)
<i>Δ_J</i>	0.0008644(59)	0.0009409(37)	0.0008809(34)	0.0007317(76)	0.000711(23)
<i>Δ_{JK}</i>	0.030321(29)	0.027688(44)	0.010711(51)	0.018425(37)	0.00145(33)
<i>Δ_K</i>	0.35015(16)	0.12535(51)	0.16689(48)	0.07804(40)	0.00533(90)
<i>δ_J</i>	0.0002610(13)	0.0002662(25)	0.0002466(42)	0.0002093(13)	0.0001813(54)
<i>δ_K</i>	0.017324(37)	0.00837(11)	0.00493(10)	−0.004733(90)	−0.00733(46)
<i>q</i>		−4209.22801(85)	−4269.5444(15)	57.397(13)	−8143.7311(48)
<i>q_J</i>		0.402620(30)	0.79620(32)	−0.37591(17)	1.20883(16)
<i>q_K</i>		12.38703(26)	11.68670(40)	0.7197(32)	21.1754(37)
<i>q_{JK}</i>			−0.002605(81)		−0.003300(91)
<i>r</i>		704.1957(25)	834.1461(20)	−125.508(17)	1564.7212(24)
<i>r_J</i>		−0.047564(89)	−0.113801(73)	0.06675(58)	−0.167319(86)
<i>r_K</i>		−5.9636(15)	−7.9354(11)	1.700(11)	−13.2566(15)
<i>χ_{aa}</i>	2.2329(15)	2.2288(22)	2.2239(18)	2.2237(17)	2.2202(21)
<i>χ_{bb} − χ_{cc}</i>	6.0557(29)	6.0476(43)	6.0476(36)	6.0364(32)	6.0480(68)
<i>χ_{ab}</i>		−0.190(12)	−0.1861(83)		−0.2061(36)
r.m.s. ^b	0.0031	0.0041	0.0034	0.0036	0.0042

^a Numbers in parentheses denote one standard uncertainty (type *A*, *k* = 1) and apply to the last digits of the parameters.^b Root-mean-square deviation of the fit in MHz.

on the relative orientation of the two methyl groups in the molecule (i.e., on information contained in the coefficients *a* and *b*), but they do depend on the fact that the two tops interact only weakly with each other (i.e., on the assumption that each one-top wavefunction symbol in Eqs. (4), e.g., ψ_{1E+} , represents exactly the same function wherever it occurs).

Similar arguments (involving somewhat higher-order terms) can be used to understand Eqs. (3), since we can add centrifugal distortion corrections in the internal-rotation angular momenta to the AJ_a^2 terms as follows:

$$(A_0 + a_1 p_1^2 + c_1 \cos 3\alpha_1 + a_2 p_2^2 + c_2 \cos 3\alpha_2) J_a^2 \quad (5)$$

and then use relations analogous to Eqs. (4) to derive Eqs. (3).

5. Global fit of all symmetry species together

On the basis of the separate analyses described above, a number of global least-squares fits of the transitions for all the symmetry species were tried using a two-top internal rotation program, which also includes nuclear quadrupole hyperfine interaction terms. Even though at least two alternative two-top programs are used in the literature [7–17], we decided to write our own (as described briefly below) in order to better understand the model and the physical and numerical approximations being used.

After exploring many sets of trial-and-error interaction operators and fitting parameters, the following Hamiltonian, which includes 7 torsion, 8 rotation, and 30 torsion–rotation terms, was found to give a satisfactory global fit:

$$\begin{aligned}
 H = & A'J_z^2 + B'J_x^2 + C'J_y^2 - \Delta_J \mathbf{J}^4 - \Delta_{JK} \mathbf{J}^2 J_z^2 - \Delta_K J_z^4 \\
 & - \delta_J 2\mathbf{J}^2 (J_x^2 - J_y^2) - \delta_K [J_z^2 (J_x^2 - J_y^2) + (J_x^2 - J_y^2) J_z^2] \\
 & + f_1 p_1^2 + f_2 p_2^2 + f_{12} p_1 p_2 + (1/2) V_{3,1} (1 - \cos 3\alpha_1) \\
 & + (1/2) V_{3,2} (1 - \cos 3\alpha_2) + V_{12c} (1 - \cos 3\alpha_1) (1 - \cos 3\alpha_2) \\
 & + V_{12s} \sin 3\alpha_1 \sin 3\alpha_2 + (q_1 + q_{1J} \mathbf{J}^2 + q_{1K} J_z^2) J_z p_1 \\
 & + (q_2 + q_{2J} \mathbf{J}^2 + q_{2K} J_z^2) J_z p_2 + (r_1 + r_{1J} \mathbf{J}^2) J_x p_1 \\
 & + (1/2) r_{1K} (J_z^2 J_x + J_x J_z^2) p_1 + (r_2 + r_{2J} \mathbf{J}^2) J_x p_2 \\
 & + (1/2) r_{2K} (J_z^2 J_x + J_x J_z^2) p_2 + (A_1 p_1^2 + A_2 p_2^2) J_z^2 \\
 & + (B_1 p_1^2 + B_2 p_2^2 + B_{12} p_1 p_2) J_x^2 \\
 & + (C_1 p_1^2 + C_2 p_2^2 + C_{12} p_1 p_2) J_y^2 - (A_{1J} p_1^2 + A_{2J} p_2^2) \mathbf{J}^4 \\
 & - (A_{1JK} p_1^2 + A_{2JK} p_2^2) \mathbf{J}^2 J_z^2 - (A_{1K} p_1^2 + A_{12K} p_1 p_2) J_z^4 \\
 & + q_{12p} p_1 p_2 (p_1 + p_2) J_z + q_{12m} p_1 p_2 (p_1 - p_2) J_z \\
 & + r_{12p} p_1 p_2 (p_1 + p_2) J_x + r_{12m} p_1 p_2 (p_1 - p_2) J_x \\
 & + H_{\text{nuclear quadrupole}}, \quad (6)
 \end{aligned}$$

where subscripts 1 and 2 indicate quantities associated with top 1 and top 2, respectively (e.g., $V_{3,1}$ and $V_{3,2}$ represent the threefold barriers of top 1 and top 2). The quantity $H_{\text{nuclear quadrupole}}$ represents the nuclear quadrupole interaction terms, taken in the usual form (e.g., Eq. (1) of [19]). In the Hamiltonian operator of Eq. (6), the axis system (*x*, *y*, *z*) is taken in such a way that the *y*-axis is perpendicular to the skeletal plane and quadratic cross terms in the angular momentum components J_x , J_y , and J_z do not occur. Furthermore, terms representing interaction between internal rotation and overall rotation are all of the kinetic-coupling type.

The Hamiltonian matrix was set up using the Hamiltonian operator above and torsion–rotation basis

functions of the form $|J, K\rangle|m_1\rangle|m_2\rangle$, where $|J, K\rangle$ is a symmetric top wavefunction and $|m_1\rangle$ and $|m_2\rangle$ represent free-rotor basis functions for top 1 and top 2, respectively, with m_1 and m_2 taking integer values (including zero). These were restricted by torsional symmetry species in the program to the following values *modulo* 3: A functions have $m_1 = m_2 = 0$; E_1 functions have $m_1 = +1, m_2 = 0$; E_2 functions have $m_1 = 0, m_2 = +1$; E_3 functions have $m_1 = +1, m_2 = -1$; and E_4 functions have $m_1 = +1, m_2 = +1$. As indicated in Table 2, labeling conventions have been chosen so that when $m_1 m_2 > 0$, the two tops generate angular momenta pointing in almost the same direction in the molecule. Nuclear hyperfine interaction terms were taken into account only for $\Delta J = 0$ matrix elements.

The torsion–rotation Hamiltonian matrix was diagonalized directly in a one-step process using torsional functions with $|m_1| \leq 12$ and $|m_2| \leq 12$. This basis set and the one-step diagonalization procedure made the least-squares fitting process rather slow (one fit of several iterations up to $J = 8$ took essentially overnight on a PC with a 700 MHz CPU). However, it also removed many possibilities for subtle programming errors, which we felt to be important since the *N*-methylacetamide spectrum represented our first attempt at treating a molecule with two low-barrier tops to kHz accuracy.

Parameters obtained from the global fit are shown in Table 3. All assigned transitions, with observed-minus-calculated residuals, are given in Table 4. The root-mean-square deviation of the fit was 3.8 kHz, which is nearly equal to the experimental measurement error.

6. Discussion of the parameters from the global fit

6.1. Transformation of quadratic-term coefficients to the PAM system

It is convenient when deducing physical meaning from the fitting parameters to transform the terms in

Table 2 quadratic in the operators J_x, J_y, J_z, p_1 , and p_2 to terms occurring in the traditional PAM Hamiltonian operator [25]:

$$H = AJ_a^2 + BJ_b^2 + CJ_c^2 + F_1(p_1 - \pi_1)^2 + F_2(p_2 - \pi_2)^2 + F_{12}[(p_1 - \pi_1)(p_2 - \pi_2) + (p_2 - \pi_2)(p_1 - \pi_1)] + V(\alpha_1, \alpha_2), \quad (7)$$

where a, b , and c represent the PAM axes. In our case $c = y$, so that

$$\pi_1 \equiv \rho_{1a}J_a + \rho_{1b}J_b, \quad (8a)$$

$$\pi_2 \equiv \rho_{2a}J_a + \rho_{2b}J_b, \quad (8b)$$

$$\rho_{1\beta} \equiv \lambda_{1\beta}I_1/I_\beta, \quad (8c)$$

$$\rho_{2\beta} \equiv \lambda_{2\beta}I_2/I_\beta, \quad (8d)$$

with $\beta = a$ or b . Also, $\lambda_{i\beta}$ with $i = 1$ or 2 is the direction cosine between the threefold symmetry axis of top i and the principal axis β of the whole molecule, and $V(\alpha_1, \alpha_2)$ is the internal rotation potential energy.

Relations between the kinetic energy parameters appearing in Eqs. (6) and (7) can be obtained by comparing coefficients of like quadratic terms in these two equations, after performing a rotation through an as yet undetermined angle θ about the y -axis, which relates the a, b, c principal axes in Eq. (7) to the x, y, z axes in Eq. (6) according to the equation

$$\begin{bmatrix} z \\ x \\ y \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}. \quad (9)$$

The relations between four pairs of parameters in Eqs. (6) and (7) do not depend on θ :

$$\begin{aligned} f_1 &= F_1, \\ f_2 &= F_2, \\ f_{12} &= 2F_{12}, \\ C' &= C. \end{aligned} \quad (10)$$

For the rest we find

Table 3

Molecular parameters^a (MHz) of *N*-methylacetamide determined from a global fit^b to the Hamiltonian in Eq. (6)

A'	11249.47(43)	$V_{3,2}$	73.468(51) ^c	r_2	−3345.53(93)	C_1	1.3086(11)
B'	3916.5540(73)	V_{12c}	0.914(27) ^c	r_{2J}	0.01993(29)	C_2	−0.07520(83)
C'	2902.7355(51)	V_{12s}	−2.989(60) ^c	r_{2K}	0.264(38)	C_{12}	0.0913(22)
Δ_J	0.000664(21)	q_1	−19769.(34)	q_{12p}	27.30(80)	Δ_{1J}	−0.0000350(59)
Δ_{JK}	−0.01050(15)	q_{1J}	−0.2048(30)	q_{12m}	41.2(14)	Δ_{2J}	0.0000263(59)
Δ_K	−0.1093(10)	q_{1K}	1.570(31)	r_{12p}	−1.292(52)	Δ_{1JK}	0.00115(25)
δ_J	0.00015687(98)	q_2	−19967.5(80)	r_{12m}	3.35(16)	Δ_{2JK}	0.00326(30)
δ_K	−0.000736(39)	q_{2J}	0.0756(34)	A_1	−43.88(89)	Δ_{1K}	0.0253(15)
f_1	5.9077(53) ^c	q_{2K}	−0.785(24)	A_2	4.19(54)	Δ_{12K}	0.0158(10)
f_2	5.5234(44) ^c	r_1	−2847.2(39)	B_1	0.260(21)	χ_{aa}	2.23660(81)
f_{12}	0.6397(24) ^c	r_{1J}	−0.01890(22)	B_2	−0.746(17)	$\chi_{bb} - \chi_{cc}$	6.0453(17)
$V_{3,1}$	79.062(93) ^c	r_{1K}	−0.209(43)	B_{12}	0.1019(53)	χ_{ab}	0.1904(28)

^a Numbers in parentheses denote one standard uncertainty (type $A, k = 1$) and apply to the last digits of the parameters.

^b Root-mean-square deviation of this global fit is 0.0038 MHz.

^c In cm^{-1} .

Table 4

Assigned transitions^a and observed-minus-calculated residuals^b from the least squares fit^c

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
A	3	2	0	2	A	2	1	0	1	13503.741	.001
A	2	2	0	2	A	2	1	0	1	13504.584	–.002
A	2	2	0	2	A	1	1	0	1	13503.914	–.003
A	1	2	0	2	A	1	1	0	1	13502.602	.001
A	1	2	0	2	A	0	1	0	1	13504.270	–.004
A	3	2	1	2	A	2	1	1	1	12613.172	.005
A	2	2	1	2	A	2	1	1	1	12614.499	.002
A	2	2	1	2	A	1	1	1	1	12613.929	.004
A	1	2	1	2	A	1	1	1	1	12611.854	–.002
A	1	2	1	2	A	0	1	1	1	12613.283	–.004
A	3	2	1	1	A	2	1	1	0	14600.038	–.001
A	2	2	1	1	A	2	1	1	0	14599.422	–.004
A	2	2	1	1	A	1	1	1	0	14600.669	.002
A	1	2	1	1	A	1	1	1	0	14601.621	.000
A	1	2	1	1	A	0	1	1	0	14598.521	.004
A	2	1	1	1	A	1	0	0	0	13463.453	.005
A	1	1	1	1	A	1	0	0	0	13464.023	.002
A	0	1	1	1	A	1	0	0	0	13462.589	.000
A	3	2	1	2	A	2	1	0	1	19273.287	.000
A	2	2	1	2	A	2	1	0	1	19274.617	.000
A	1	2	1	2	A	2	1	0	1	19272.547	.000
A	2	2	1	2	A	1	1	0	1	19273.946	–.002
A	1	2	1	2	A	1	1	0	1	19271.874	–.004
A	1	2	1	2	A	0	1	0	1	19273.550	–.001
A	3	2	2	1	A	3	2	1	2	22956.321	–.008
A	2	2	2	1	A	3	2	1	2	22955.601	–.011
A	3	2	2	1	A	2	2	1	2	22954.999	.000
A	2	2	2	1	A	2	2	1	2	22954.280	–.002
A	1	2	2	1	A	2	2	1	2	22955.395	–.002
A	2	2	2	1	A	1	2	1	2	22956.355	.004
A	1	2	2	1	A	1	2	1	2	22957.468	.001
A	3	2	2	0	A	3	2	1	1	20078.854	.004
A	2	2	2	0	A	3	2	1	1	20078.001	–.002
A	3	2	2	0	A	2	2	1	1	20079.465	.003
A	2	2	2	0	A	2	2	1	1	20078.616	.000
A	1	2	2	0	A	2	2	1	1	20079.933	.001
A	2	2	2	0	A	1	2	1	1	20077.662	.000
A	1	2	2	0	A	1	2	1	1	20078.970	–.008
A	4	3	0	3	A	3	2	0	2	20005.145	.002
A	3	3	0	3	A	3	2	0	2	20006.214	.002
A	3	3	0	3	A	2	2	0	2	20005.365	–.001
A	2	3	0	3	A	2	2	0	2	20003.920	–.003
A	2	3	0	3	A	1	2	0	2	20005.237	–.002
A	5	4	0	4	A	4	3	0	3	26243.524	.004
A	4	4	0	4	A	3	3	0	3	26243.778	.002
A	4	3	1	3	A	3	2	1	2	18858.545	.001
A	3	3	1	3	A	3	2	1	2	18860.151	.003
A	3	3	1	3	A	2	2	1	2	18858.819	.001
A	2	3	1	3	A	2	2	1	2	18856.650	–.001
A	2	3	1	3	A	1	2	1	2	18858.719	–.002
A	5	4	1	4	A	4	3	1	3	25039.149	.003
A	4	4	1	4	A	3	3	1	3	25039.318	.003
A	3	4	1	4	A	2	3	1	3	25039.251	–.002
A	4	3	1	2	A	3	2	1	1	21831.971	.002
A	3	3	1	2	A	2	2	1	1	21832.179	.001
A	2	3	1	2	A	1	2	1	1	21831.771	.000
A	4	3	0	3	A	3	2	1	2	14235.598	.001
A	3	3	0	3	A	3	2	1	2	14236.667	.001
A	3	3	0	3	A	2	2	1	2	14235.334	–.001
A	2	3	0	3	A	2	2	1	2	14233.886	–.007
A	2	3	0	3	A	1	2	1	2	14235.965	.003
A	5	4	0	4	A	4	3	1	3	21620.577	.003

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
A	4	4	0	4	A	4	3	1	3	21621.901	.002
A	4	4	0	4	A	3	3	1	3	21620.296	.002
A	3	4	0	4	A	3	3	1	3	21618.627	–.002
A	3	4	0	4	A	2	3	1	3	21620.795	.001
A	4	3	1	3	A	3	2	0	2	24628.092	.003
A	3	3	1	3	A	3	2	0	2	24629.696	.002
A	3	3	1	3	A	2	2	0	2	24628.850	.002
A	2	3	1	3	A	2	2	0	2	24626.679	–.004
A	2	3	1	3	A	1	2	0	2	24628.001	.003
A	4	3	1	2	A	4	3	0	3	10576.926	.002
A	3	3	1	2	A	4	3	0	3	10576.518	–.002
A	4	3	1	2	A	3	3	0	3	10575.861	.005
A	3	3	1	2	A	3	3	0	3	10575.450	–.001
A	2	3	1	2	A	3	3	0	3	10575.997	.000
A	3	3	1	2	A	2	3	0	3	10576.896	.002
A	2	3	1	2	A	2	3	0	3	10577.441	.001
A	5	4	1	3	A	5	4	0	4	13305.902	.000
A	4	4	1	3	A	5	4	0	4	13305.642	.001
A	5	4	1	3	A	4	4	0	4	13304.566	–.011
A	4	4	1	3	A	4	4	0	4	13304.314	–.002
A	3	4	1	3	A	4	4	0	4	13304.644	–.001
A	4	4	1	3	A	3	4	0	4	13305.978	–.003
A	3	4	1	3	A	3	4	0	4	13306.311	.001
A	6	5	1	4	A	6	5	0	5	17058.273	.003
A	5	5	1	4	A	6	5	0	5	17058.154	.001
A	5	5	1	4	A	5	5	0	5	17056.570	–.001
A	4	5	1	4	A	4	5	0	5	17058.616	–.001
A	7	6	1	5	A	7	6	0	6	21820.822	.006
A	6	6	1	5	A	6	6	0	6	21819.062	.004
A	5	6	1	5	A	5	6	0	6	21821.122	.009
A	4	3	2	2	A	3	2	2	1	20409.346	–.001
A	3	3	2	2	A	2	2	2	1	20410.065	.001
A	2	3	2	2	A	1	2	2	1	20408.953	.004
A	4	3	2	2	A	4	3	1	3	24507.135	.002
A	3	3	2	2	A	3	3	1	3	24505.530	.002
A	2	3	2	2	A	2	3	1	3	24507.701	.007
A	4	3	2	1	A	3	2	2	0	20814.416	.001
A	3	3	2	1	A	2	2	2	0	20814.941	.005
A	2	3	2	1	A	1	2	2	0	20814.060	.001
A	4	3	2	1	A	4	3	1	2	19061.300	.006
A	3	3	2	1	A	4	3	1	2	19060.971	.002
A	4	3	2	1	A	3	3	1	2	19061.702	.003
A	3	3	2	1	A	3	3	1	2	19061.372	–.002
A	2	3	2	1	A	3	3	1	2	19061.811	–.002
A	3	3	2	1	A	2	3	1	2	19060.821	–.006
A	2	3	2	1	A	2	3	1	2	19061.258	–.008
A	5	4	2	2	A	5	4	1	3	18190.602	.001
A	5	4	2	2	A	4	4	1	3	18190.860	–.002
A	4	4	2	2	A	4	4	1	3	18190.643	.008
A	3	4	2	2	A	4	4	1	3	18190.924	.003
A	4	4	2	2	A	3	4	1	3	18190.305	–.001
A	3	4	2	2	A	3	4	1	3	18190.602	.010
A	6	5	2	3	A	6	5	1	4	17792.584	.000
A	5	5	2	3	A	5	5	1	4	17792.443	.003
A	4	5	2	3	A	4	5	1	4	17792.624	.011
A	7	6	2	4	A	7	6	1	5	18151.447	.003
A	6	6	2	4	A	6	6	1	5	18151.080	.000
A	5	6	2	4	A	5	6	1	5	18151.508	.002
A	8	7	2	5	A	8	7	1	6	19485.405	.001
A	7	7	2	5	A	7	7	1	6	19484.810	–.004
A	9	8	2	6	A	9	8	1	7	21953.423	–.002
A	8	8	2	6	A	8	8	1	7	21952.614	–.008
A	7	8	2	6	A	7	8	1	7	21953.518	–.009
A	5	4	1	3	A	4	3	2	2	10419.344	.001

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	$\text{o} - \text{c}$
A	4	4	1	3	A	3	3	2	2	10419.085	.003
A	3	4	1	3	A	2	3	2	2	10419.419	.008
A	6	5	1	4	A	5	4	2	3	19262.715	.001
A	5	5	1	4	A	4	4	2	3	19262.260	-.001
A	4	5	1	4	A	3	4	2	3	19262.825	.000
E_1	9	8	2	6	E_1	9	8	1	7	24593.559	.005
E_1	8	8	2	6	E_1	8	8	1	7	24592.964	.001
E_1	7	8	2	6	E_1	7	8	1	7	24593.627	-.002
E_1	3	2	0	2	E_1	2	1	0	1	13338.733	.000
E_1	2	2	0	2	E_1	2	1	0	1	13339.517	-.004
E_1	2	2	0	2	E_1	1	1	0	1	13338.902	-.005
E_1	1	2	0	2	E_1	1	1	0	1	13337.677	-.004
E_1	1	2	0	2	E_1	0	1	0	1	13339.216	.000
E_1	4	3	0	3	E_1	3	2	0	2	19839.145	-.001
E_1	3	3	0	3	E_1	3	2	0	2	19840.165	-.002
E_1	3	3	0	3	E_1	2	2	0	2	19839.378	-.002
E_1	2	3	0	3	E_1	2	2	0	2	19837.995	-.005
E_1	2	3	0	3	E_1	1	2	0	2	19839.218	-.008
E_1	5	4	0	4	E_1	4	3	0	3	26088.510	-.001
E_1	4	4	0	4	E_1	3	3	0	3	26088.787	-.001
E_1	3	4	0	4	E_1	2	3	0	3	26088.536	.002
E_1	3	2	0	2	E_1	2	1	1	1	10576.202	-.003
E_1	2	2	0	2	E_1	2	1	1	1	10577.000	.007
E_1	2	2	0	2	E_1	1	1	1	1	10577.167	.006
E_1	4	3	0	3	E_1	3	2	1	2	16995.975	-.001
E_1	3	3	0	3	E_1	3	2	1	2	16996.998	.000
E_1	3	3	0	3	E_1	2	2	1	2	16996.245	-.001
E_1	2	3	0	3	E_1	2	2	1	2	16994.863	-.003
E_1	5	4	0	4	E_1	4	3	1	3	23470.945	-.001
E_1	4	4	0	4	E_1	4	3	1	3	23472.243	-.003
E_1	4	4	0	4	E_1	3	3	1	3	23470.997	-.003
E_1	3	4	0	4	E_1	3	3	1	3	23469.363	-.003
E_1	3	4	0	4	E_1	2	3	1	3	23471.041	-.008
E_1	5	4	0	4	E_1	4	3	1	2	13249.669	-.002
E_1	4	4	0	4	E_1	3	3	1	2	13250.921	-.002
E_1	3	4	0	4	E_1	2	3	1	2	13249.352	-.002
E_1	6	5	0	5	E_1	5	4	1	3	17105.689	.000
E_1	5	5	0	5	E_1	4	4	1	3	17107.227	-.003
E_1	4	5	0	5	E_1	3	4	1	3	17105.372	-.005
E_1	7	6	0	6	E_1	6	5	1	4	19698.025	.000
E_1	6	6	0	6	E_1	5	5	1	4	19699.766	.001
E_1	5	6	0	6	E_1	4	5	1	4	19697.734	.000
E_1	3	2	1	2	E_1	2	1	1	1	13419.377	.003
E_1	2	2	1	2	E_1	2	1	1	1	13420.128	.001
E_1	2	2	1	2	E_1	1	1	1	1	13420.297	.002
E_1	1	2	1	2	E_1	1	1	1	1	13419.123	-.002
E_1	1	2	1	2	E_1	0	1	1	1	13418.705	.001
E_1	4	3	1	3	E_1	3	2	1	2	19613.543	.003
E_1	3	3	1	3	E_1	3	2	1	2	19614.788	.002
E_1	3	3	1	3	E_1	2	2	1	2	19614.036	.002
E_1	2	3	1	3	E_1	2	2	1	2	19612.353	.001
E_1	2	3	1	3	E_1	1	2	1	2	19613.520	-.002
E_1	5	4	1	4	E_1	4	3	1	3	25568.156	-.001
E_1	4	4	1	4	E_1	3	3	1	3	25568.489	.002
E_1	3	4	1	4	E_1	2	3	1	3	25568.190	.003
E_1	3	2	1	1	E_1	2	1	1	0	13844.279	-.004
E_1	2	2	1	1	E_1	1	1	1	0	13844.767	.001
E_1	1	2	1	1	E_1	1	1	1	0	13844.716	.009
E_1	1	2	1	1	E_1	0	1	1	0	13843.591	-.001
E_1	4	3	1	2	E_1	3	2	1	1	21016.205	-.001
E_1	3	3	1	2	E_1	2	2	1	1	21016.213	-.003
E_1	2	3	1	2	E_1	1	2	1	1	21016.213	.002
E_1	3	2	1	1	E_1	2	1	1	1	22237.985	.002
E_1	2	2	1	1	E_1	2	1	1	1	22238.032	.010

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	$\text{o} - \text{c}$
E_1	2	2	1	1	E_1	1	1	1	1	22238.193	.003
E_1	1	2	1	1	E_1	1	1	1	1	22238.137	.006
E_1	1	2	1	1	E_1	0	1	1	1	22237.715	.005
E_1	4	3	1	2	E_1	4	3	1	3	10221.273	-.002
E_1	3	3	1	2	E_1	3	3	1	3	10220.076	-.001
E_1	2	3	1	2	E_1	2	3	1	3	10221.694	.000
E_1	5	4	1	3	E_1	5	4	1	4	12869.440	-.005
E_1	4	4	1	3	E_1	4	4	1	4	12867.899	-.004
E_1	3	4	1	3	E_1	3	4	1	4	12869.842	.000
E_1	6	5	1	4	E_1	6	5	1	5	16693.076	.001
E_1	5	5	1	4	E_1	5	5	1	5	16691.342	-.006
E_1	4	5	1	4	E_1	4	5	1	5	16693.424	-.002
E_1	4	3	1	3	E_1	3	2	1	1	10794.932	.001
E_1	3	3	1	3	E_1	2	2	1	1	10796.139	.000
E_1	2	3	1	3	E_1	1	2	1	1	10794.515	-.001
E_1	5	4	1	4	E_1	4	3	1	2	15346.885	.003
E_1	4	4	1	4	E_1	3	3	1	2	15348.413	.003
E_1	3	4	1	4	E_1	2	3	1	2	15346.491	-.002
E_1	6	5	1	5	E_1	5	4	1	3	18591.298	.003
E_1	5	5	1	5	E_1	4	4	1	3	18593.059	-.001
E_1	4	5	1	5	E_1	3	4	1	3	18590.938	-.001
E_1	7	6	1	6	E_1	6	5	1	4	20657.889	.005
E_1	6	6	1	6	E_1	5	5	1	4	20659.767	-.004
E_1	5	6	1	6	E_1	4	5	1	4	20657.563	-.005
E_1	3	2	1	2	E_1	2	1	0	1	16181.900	-.002
E_1	2	2	1	2	E_1	2	1	0	1	16182.651	-.004
E_1	1	2	1	2	E_1	2	1	0	1	16181.475	-.010
E_1	2	2	1	2	E_1	1	1	0	1	16182.038	-.003
E_1	1	2	1	2	E_1	1	1	0	1	16180.866	-.005
E_1	1	2	1	2	E_1	0	1	0	1	16182.402	-.004
E_1	4	3	1	3	E_1	3	2	0	2	22456.711	.001
E_1	3	3	1	3	E_1	3	2	0	2	22457.956	.000
E_1	3	3	1	3	E_1	2	2	0	2	22457.166	-.002
E_1	2	3	1	3	E_1	2	2	0	2	22455.484	-.001
E_1	2	3	1	3	E_1	1	2	0	2	22456.711	.000
E_1	2	1	1	0	E_1	1	0	0	0	17846.606	.000
E_1	1	1	1	0	E_1	1	0	0	0	17846.159	-.002
E_1	0	1	1	0	E_1	1	0	0	0	17847.273	-.002
E_1	3	2	1	1	E_1	2	1	0	1	25000.511	-.001
E_1	2	2	1	1	E_1	1	1	0	1	24999.933	-.003
E_1	1	2	1	1	E_1	1	1	0	1	24999.866	-.010
E_1	1	2	1	1	E_1	0	1	0	1	25001.412	.001
E_1	2	1	1	0	E_1	2	1	0	1	11156.230	.001
E_1	1	1	1	0	E_1	2	1	0	1	11155.785	.001
E_1	2	1	1	0	E_1	1	1	0	1	11155.613	-.002
E_1	1	1	1	0	E_1	1	1	0	1	11155.166	-.004
E_1	0	1	1	0	E_1	1	1	0	1	11156.276	-.008
E_1	1	1	1	0	E_1	0	1	0	1	11156.704	-.001
E_1	3	2	1	1	E_1	3	2	0	2	11661.779	.000
E_1	2	2	1	1	E_1	3	2	0	2	11661.805	-.012
E_1	3	2	1	1	E_1	2	2	0	2	11660.999	.008
E_1	2	2	1	1	E_1	2	2	0	2	11661.028	-.001
E_1	1	2	1	1	E_1	2	2	0	2	11660.969	-.001
E_1	2	2	1	1	E_1	1	2	0	2	11662.263	.008
E_1	1	2	1	1	E_1	1	2	0	2	11662.194	-.001
E_1	4	3	1	2	E_1	4	3	0	3	12838.842	.003
E_1	3	3	1	2	E_1	3	3	0	3	12837.866	.001
E_1	2	3	1	2	E_1	2	3	0	3	12839.182	.002
E_1	5	4	1	3	E_1	5	4	0	4	14966.655	-.001
E_1	4	4	1	3	E_1	4	4	0	4	14965.391	-.001
E_1	3	4	1	3	E_1	3	4	0	4	14966.979	-.002
E_1	6	5	1	4	E_1	6	5	0	5	18178.680	-.002
E_1	5	5	1	4	E_1	5	5	0	5	18177.179	.001
E_1	4	5	1	4	E_1	4	5	0	5	18178.988	.000

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
E_1	7	6	1	5	E_1	7	6	0	6	22466.061	.002
E_1	6	6	1	5	E_1	6	6	0	6	22464.414	.002
E_1	5	6	1	5	E_1	5	6	0	6	22466.342	.005
E_1	6	5	1	4	E_1	5	4	2	2	12133.453	.000
E_1	5	5	1	4	E_1	4	4	2	2	12133.453	.000
E_1	4	5	1	4	E_1	3	4	2	2	12133.453	–.004
E_1	7	6	1	5	E_1	6	5	2	3	19636.735	.000
E_1	6	6	1	5	E_1	5	5	2	3	19636.792	.006
E_1	5	6	1	5	E_1	4	5	2	3	19636.735	.005
E_1	5	4	1	3	E_1	4	3	2	2	20809.539	–.007
E_1	4	4	1	3	E_1	3	3	2	2	20809.811	–.001
E_1	3	4	1	3	E_1	2	3	2	2	20809.462	.005
E_1	6	5	1	5	E_1	5	4	2	3	11569.353	.001
E_1	5	5	1	5	E_1	4	4	2	3	11571.176	.001
E_1	4	3	2	2	E_1	3	2	2	1	20727.149	–.007
E_1	3	3	2	2	E_1	3	2	2	1	20726.924	–.001
E_1	3	3	2	2	E_1	2	2	2	1	20727.733	.003
E_1	2	3	2	2	E_1	1	2	2	1	20726.789	.001
E_1	4	3	2	1	E_1	3	2	2	0	20562.553	–.005
E_1	3	3	2	1	E_1	2	2	2	0	20563.189	–.001
E_1	2	3	2	1	E_1	1	2	2	0	20562.180	.002
E_1	5	4	2	2	E_1	5	4	2	3	16128.974	.001
E_1	4	4	2	2	E_1	4	4	2	3	16129.069	–.001
E_1	3	4	2	2	E_1	3	4	2	3	16128.938	–.010
E_1	6	5	2	3	E_1	6	5	2	4	15900.423	–.001
E_1	5	5	2	3	E_1	5	5	2	4	15900.423	.011
E_1	4	5	2	3	E_1	4	5	2	4	15900.423	–.003
E_1	3	2	2	1	E_1	3	2	0	2	19357.609	–.001
E_1	2	2	2	1	E_1	2	2	0	2	19356.017	.001
E_1	1	2	2	1	E_1	1	2	0	2	19358.499	.003
E_1	4	3	2	2	E_1	4	3	0	3	20245.620	.000
E_1	3	3	2	2	E_1	3	3	0	3	20244.367	.000
E_1	2	3	2	2	E_1	2	3	0	3	20246.058	.000
E_1	5	4	2	3	E_1	5	4	0	4	21988.599	.000
E_1	4	4	2	3	E_1	4	4	0	4	21987.273	–.002
E_1	3	4	2	3	E_1	3	4	0	4	21988.936	–.004
E_1	3	2	2	1	E_1	2	1	1	0	21540.117	.003
E_1	2	2	2	1	E_1	1	1	1	0	21539.756	.003
E_1	1	2	2	1	E_1	0	1	1	0	21539.902	.009
E_1	3	2	2	1	E_1	3	2	1	2	16514.441	.001
E_1	2	2	2	1	E_1	3	2	1	2	16513.643	.008
E_1	3	2	2	1	E_1	2	2	1	2	16513.681	–.007
E_1	2	2	2	1	E_1	2	2	1	2	16512.885	.003
E_1	1	2	2	1	E_1	2	2	1	2	16514.138	.002
E_1	2	2	2	1	E_1	1	2	1	2	16514.057	.005
E_1	1	2	2	1	E_1	1	2	1	2	16515.310	.004
E_1	4	3	2	2	E_1	4	3	1	3	17628.056	.001
E_1	3	3	2	2	E_1	4	3	1	3	17627.825	.000
E_1	4	3	2	2	E_1	3	3	1	3	17626.814	.004
E_1	3	3	2	2	E_1	3	3	1	3	17626.579	.000
E_1	2	3	2	2	E_1	3	3	1	3	17626.888	–.002
E_1	3	3	2	2	E_1	2	3	1	3	17628.257	–.004
E_1	2	3	2	2	E_1	2	3	1	3	17628.573	.001
E_1	5	4	2	3	E_1	5	4	1	4	19891.385	–.004
E_1	5	4	2	3	E_1	4	4	1	4	19889.815	.002
E_1	4	4	2	3	E_1	4	4	1	4	19889.783	–.004
E_1	3	4	2	3	E_1	4	4	1	4	19889.815	–.004
E_1	3	4	2	3	E_1	3	4	1	4	19891.797	–.004
E_1	6	5	2	4	E_1	6	5	1	5	23319.996	–.004
E_1	5	5	2	4	E_1	5	5	1	5	23318.323	–.004
E_1	4	5	2	4	E_1	4	5	1	5	23320.338	–.002
E_1	3	2	2	0	E_1	3	2	1	1	24275.317	.008
E_1	2	2	2	0	E_1	2	2	1	1	24274.499	.000
E_1	1	2	2	0	E_1	1	2	1	1	24275.760	.001

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
E_1	4	3	2	1	E_1	4	3	1	2	23821.664	.003
E_1	3	3	2	1	E_1	3	3	1	2	23821.473	.000
E_1	2	3	2	1	E_1	3	3	1	2	23821.664	.002
E_1	2	3	2	1	E_1	2	3	1	2	23821.723	–.004
E_1	5	4	2	2	E_1	5	4	1	3	23150.915	–.002
E_1	4	4	2	2	E_1	4	4	1	3	23150.956	.001
E_1	3	4	2	2	E_1	3	4	1	3	23150.905	–.002
E_1	6	5	2	3	E_1	6	5	1	4	22527.347	–.002
E_1	5	5	2	3	E_1	5	5	1	4	22527.393	.001
E_1	4	5	2	3	E_1	4	5	1	4	22527.338	–.002
E_1	7	6	2	4	E_1	7	6	1	5	22314.874	.000
E_1	6	6	2	4	E_1	6	6	1	5	22314.774	–.001
E_1	5	6	2	4	E_1	5	6	1	5	22314.893	.002
E_1	8	7	2	5	E_1	8	7	1	6	22900.792	.002
E_1	7	7	2	5	E_1	7	7	1	6	22900.461	.002
E_1	6	7	2	5	E_1	6	7	1	6	22900.840	.002
E_2	7	6	0	6	E_2	6	5	1	4	19652.947	.005
E_2	6	6	0	6	E_2	5	5	1	4	19654.645	.000
E_2	5	6	0	6	E_2	4	5	1	4	19652.653	–.005
E_2	9	8	2	6	E_2	9	8	1	7	24842.008	.011
E_2	8	8	2	6	E_2	8	8	1	7	24841.449	.008
E_2	7	8	2	6	E_2	7	8	1	7	24842.076	.009
E_2	3	2	0	2	E_2	2	1	0	1	13276.140	.002
E_2	2	2	0	2	E_2	2	1	0	1	13276.899	–.002
E_2	2	2	0	2	E_2	1	1	0	1	13276.304	–.002
E_2	1	2	0	2	E_2	1	1	0	1	13275.113	–.006
E_2	1	2	0	2	E_2	0	1	0	1	13276.607	.001
E_2	4	3	0	3	E_2	3	2	0	2	19789.789	.000
E_2	3	3	0	3	E_2	3	2	0	2	19790.781	.000
E_2	3	3	0	3	E_2	2	2	0	2	19790.019	.000
E_2	2	3	0	3	E_2	2	2	0	2	19788.676	–.002
E_2	2	3	0	3	E_2	1	2	0	2	19789.858	–.007
E_2	5	4	0	4	E_2	4	3	0	3	26062.753	–.001
E_2	4	4	0	4	E_2	3	3	0	3	26063.031	.000
E_2	3	4	0	4	E_2	2	3	0	3	26062.778	.003
E_2	3	2	0	2	E_2	2	1	1	1	10487.247	.002
E_2	2	2	0	2	E_2	2	1	1	1	10488.003	–.005
E_2	2	2	0	2	E_2	1	1	1	1	10488.160	.002
E_2	1	2	0	2	E_2	1	1	1	1	10486.970	–.001
E_2	1	2	0	2	E_2	0	1	1	1	10486.606	.010
E_2	4	3	0	3	E_2	3	2	1	2	16846.486	.002
E_2	3	3	0	3	E_2	3	2	1	2	16847.473	–.003
E_2	3	3	0	3	E_2	2	2	1	2	16846.707	.001
E_2	2	3	0	3	E_2	2	2	1	2	16845.364	–.002
E_2	2	3	0	3	E_2	1	2	1	2	16846.554	–.010
E_2	5	4	0	4	E_2	4	3	1	3	23309.347	.001
E_2	4	4	0	4	E_2	4	3	1	3	23310.615	–.001
E_2	4	4	0	4	E_2	3	3	1	3	23309.357	.000
E_2	3	4	0	4	E_2	3	3	1	3	23307.758	–.003
E_2	3	4	0	4	E_2	2	3	1	3	23309.455	–.006
E_2	5	4	0	4	E_2	4	3	1	2	13023.564	–.002
E_2	4	4	0	4	E_2	3	3	1	2	13024.768	–.003
E_2	3	4	0	4	E_2	2	3	1	2	13023.259	–.003
E_2	6	5	0	5	E_2	5	4	1	3	16945.519	.001
E_2	5	5	0	5	E_2	4	4	1	3	16947.010	.000
E_2	4	5	0	5	E_2	3	4	1	3	16945.213	–.004
E_2	3	2	1	2	E_2	2	1	1	1	13430.549	–.001
E_2	2	2	1	2	E_2	2	1	1	1	13431.317	–.003
E_2	2	2	1	2	E_2	1	1	1	1	13431.470	.000
E_2	1	2	1	2	E_2	1	1	1	1	13430.266	–.006
E_2	1	2	1	2	E_2	0	1	1	1	13429.894	–.003
E_2	4	3	1	3	E_2	3	2	1	2	19599.891	.000
E_2	3	3	1	3	E_2	3	2	1	2	19601.149	–.001
E_2	3	3	1	3	E_2	2	2	1	2	19600.379	–.001

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	$\text{o} - \text{c}$
E_2	2	3	1	3	E_2	2	2	1	2	19598.677	-.003
E_2	2	3	1	3	E_2	1	2	1	2	19599.875	-.004
E_2	5	4	1	4	E_2	4	3	1	3	25539.905	-.001
E_2	4	4	1	4	E_2	3	3	1	3	25540.231	.001
E_2	3	4	1	4	E_2	2	3	1	3	25539.942	.002
E_2	3	2	1	1	E_2	2	1	1	0	13837.848	-.001
E_2	2	2	1	1	E_2	1	1	1	0	13838.337	-.001
E_2	1	2	1	1	E_2	1	1	1	0	13838.274	.004
E_2	1	2	1	1	E_2	0	1	1	0	13837.156	-.001
E_2	4	3	1	2	E_2	3	2	1	1	20988.555	.000
E_2	3	3	1	2	E_2	2	2	1	1	20988.578	.003
E_2	4	3	1	2	E_2	4	3	1	3	10285.781	.000
E_2	3	3	1	2	E_2	3	3	1	3	10284.586	.000
E_2	2	3	1	2	E_2	2	3	1	3	10286.200	.001
E_2	5	4	1	3	E_2	5	4	1	4	12889.874	.001
E_2	4	4	1	3	E_2	4	4	1	4	12888.351	.003
E_2	3	4	1	3	E_2	3	4	1	4	12890.264	-.001
E_2	6	5	1	4	E_2	6	5	1	5	16630.773	.001
E_2	5	5	1	4	E_2	5	5	1	5	16629.056	-.007
E_2	4	5	1	4	E_2	4	5	1	5	16631.120	-.001
E_2	3	2	1	1	E_2	2	1	1	1	22327.667	.000
E_2	2	2	1	1	E_2	1	1	1	1	22327.862	.001
E_2	1	2	1	1	E_2	0	1	1	1	22327.417	-.001
E_2	4	3	1	3	E_2	3	2	1	1	10702.777	.003
E_2	3	3	1	3	E_2	2	2	1	1	10703.986	-.003
E_2	2	3	1	3	E_2	1	2	1	1	10702.358	.000
E_2	5	4	1	4	E_2	4	3	1	2	15254.124	-.001
E_2	4	4	1	4	E_2	3	3	1	2	15255.642	-.001
E_2	3	4	1	4	E_2	2	3	1	2	15253.736	-.005
E_2	6	5	1	5	E_2	5	4	1	3	18539.609	.001
E_2	5	5	1	5	E_2	4	4	1	3	18541.348	-.001
E_2	4	5	1	5	E_2	3	4	1	3	18539.249	-.007
E_2	7	6	1	6	E_2	6	5	1	4	20690.459	.001
E_2	6	6	1	6	E_2	5	5	1	4	20692.327	.003
E_2	5	6	1	6	E_2	4	5	1	4	20690.146	.000
E_2	3	2	1	2	E_2	2	1	0	1	16219.443	.000
E_2	2	2	1	2	E_2	2	1	0	1	16220.210	-.003
E_2	2	2	1	2	E_2	1	1	0	1	16219.614	-.004
E_2	1	2	1	2	E_2	1	1	0	1	16218.416	-.004
E_2	1	2	1	2	E_2	0	1	0	1	16219.912	.005
E_2	4	3	1	3	E_2	3	2	0	2	22543.198	.002
E_2	3	3	1	3	E_2	3	2	0	2	22544.452	-.003
E_2	3	3	1	3	E_2	2	2	0	2	22543.690	-.002
E_2	2	3	1	3	E_2	2	2	0	2	22541.989	-.003
E_2	2	3	1	3	E_2	1	2	0	2	22543.176	-.004
E_2	2	1	1	0	E_2	2	1	0	1	11278.712	.001
E_2	1	1	1	0	E_2	2	1	0	1	11278.266	.000
E_2	2	1	1	0	E_2	1	1	0	1	11278.115	-.001
E_2	1	1	1	0	E_2	1	1	0	1	11277.669	-.002
E_2	0	1	1	0	E_2	1	1	0	1	11278.776	-.008
E_2	1	1	1	0	E_2	0	1	0	1	11279.158	-.001
E_2	3	2	1	1	E_2	3	2	0	2	11840.422	.000
E_2	2	2	1	1	E_2	2	2	0	2	11839.701	-.002
E_2	1	2	1	1	E_2	1	2	0	2	11840.820	-.002
E_2	4	3	1	2	E_2	4	3	0	3	13039.188	-.001
E_2	3	3	1	2	E_2	3	3	0	3	13038.257	-.003
E_2	2	3	1	2	E_2	3	3	0	3	13038.169	-.004
E_2	3	3	1	2	E_2	2	3	0	3	13039.596	-.005
E_2	2	3	1	2	E_2	2	3	0	3	13039.512	-.001
E_2	5	4	1	3	E_2	5	4	0	4	15120.435	.003
E_2	4	4	1	3	E_2	5	4	0	4	15120.486	-.005
E_2	4	4	1	3	E_2	4	4	0	4	15119.222	.001
E_2	3	4	1	3	E_2	3	4	0	4	15120.744	.000
E_2	6	5	1	4	E_2	6	5	0	5	18224.863	.001

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o - c
E_2	5	5	1	4	E_2	5	5	0	5	18223.405	.003
E_2	4	5	1	4	E_2	4	5	0	5	18225.162	.003
E_2	7	6	1	5	E_2	7	6	0	6	22389.388	-.003
E_2	6	6	1	5	E_2	6	6	0	6	22387.769	.000
E_2	5	6	1	5	E_2	5	6	0	6	22389.660	-.004
E_2	2	1	1	0	E_2	1	0	0	0	17920.515	.002
E_2	1	1	1	0	E_2	1	0	0	0	17920.068	.000
E_2	0	1	1	0	E_2	1	0	0	0	17921.180	.000
E_2	3	2	1	1	E_2	2	1	0	1	25116.559	-.001
E_2	2	2	1	1	E_2	1	1	0	1	25116.008	-.001
E_2	1	2	1	1	E_2	0	1	0	1	25117.429	.001
E_2	4	3	1	2	E_2	3	2	2	1	13443.718	.001
E_2	3	3	1	2	E_2	2	2	2	1	13444.589	.002
E_2	2	3	1	2	E_2	1	2	2	1	13443.253	.006
E_2	5	4	1	3	E_2	4	3	2	2	20856.941	-.005
E_2	4	4	1	3	E_2	3	3	2	2	20857.235	-.001
E_2	3	4	1	3	E_2	2	3	2	2	20856.852	.003
E_2	6	5	1	5	E_2	5	4	2	3	11552.475	.008
E_2	5	5	1	5	E_2	4	4	2	3	11554.299	.004
E_2	4	5	1	5	E_2	3	4	2	3	11552.100	.007
E_2	6	5	1	4	E_2	5	4	2	2	11876.209	-.002
E_2	5	5	1	4	E_2	4	4	2	2	11876.233	.005
E_2	7	6	1	5	E_2	6	5	2	3	19289.523	-.005
E_2	6	6	1	5	E_2	5	5	2	3	19289.587	.004
E_2	5	6	1	5	E_2	4	5	2	3	19289.514	-.009
E_2	4	3	2	2	E_2	3	2	2	1	20730.768	-.002
E_2	3	3	2	2	E_2	2	2	2	1	20731.342	.000
E_2	2	3	2	2	E_2	1	2	2	1	20730.405	.001
E_2	4	3	2	1	E_2	3	2	2	0	20544.246	-.002
E_2	3	3	2	1	E_2	2	2	2	0	20544.882	.001
E_2	2	3	2	1	E_2	1	2	2	0	20543.871	.003
E_2	6	5	2	3	E_2	6	5	2	4	16033.142	-.003
E_2	5	5	2	3	E_2	5	5	2	4	16033.142	.007
E_2	4	5	2	3	E_2	4	5	2	4	16033.142	-.005
E_2	4	3	2	2	E_2	4	3	0	3	20326.243	.002
E_2	3	3	2	2	E_2	3	3	0	3	20325.020	.004
E_2	2	3	2	2	E_2	2	3	0	3	20326.670	.000
E_2	5	4	2	3	E_2	5	4	0	4	22107.574	.001
E_2	4	4	2	3	E_2	4	4	0	4	22106.279	.004
E_2	3	4	2	3	E_2	3	4	0	4	22107.909	.002
E_2	3	2	2	1	E_2	3	2	1	2	16441.955	.000
E_2	2	2	2	1	E_2	3	2	1	2	16441.144	-.006
E_2	3	2	2	1	E_2	2	2	1	2	16441.200	.015
E_2	2	2	2	1	E_2	2	2	1	2	16440.381	.001
E_2	1	2	2	1	E_2	2	2	1	2	16441.629	-.003
E_2	2	2	2	1	E_2	1	2	1	2	16441.581	.003
E_2	1	2	2	1	E_2	1	2	1	2	16442.827	-.004
E_2	4	3	2	2	E_2	4	3	1	3	17572.838	.004
E_2	3	3	2	2	E_2	4	3	1	3	17572.606	.005
E_2	4	3	2	2	E_2	3	3	1	3	17571.577	.002
E_2	3	3	2	2	E_2	3	3	1	3	17571.346	.004
E_2	2	3	2	2	E_2	3	3	1	3	17571.651	-.005
E_2	3	3	2	2	E_2	2	3	1	3	17573.034	-.008
E_2	2	3	2	2	E_2	2	3	1	3	17573.361	.005
E_2	5	4	2	3	E_2	5	4	1	4	19877.012	-.001
E_2	4	4	2	3	E_2	4	4	1	4	19875.404	.001
E_2	3	4	2	3	E_2	4	4	1	4	19875.445	.007
E_2	3	4	2	3	E_2	3	4	1	4	19877.431	.003
E_2	6	5	2	4	E_2	6	5	1	5	23350.428	-.005
E_2	5	5	2	4	E_2	5	5	1	5	23348.755	-.004
E_2	4	5	2	4	E_2	4	5	1	5	23350.771	-.003
E_2	3	2	2	0	E_2	3	2	1	1	24361.390	.005
E_2	2	2	2	0	E_2	2	2	1	1	24360.571	.002
E_2	1	2	2	0	E_2	1	2	1	1	24361.839	.000

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
E_2	4	3	2	1	E_2	4	3	1	2	23917.083	.004
E_2	3	3	2	1	E_2	3	3	1	2	23916.877	.003
E_2	2	3	2	1	E_2	2	3	1	2	23917.147	–.003
E_2	5	4	2	2	E_2	5	4	1	3	23294.169	.000
E_2	4	4	2	2	E_2	4	4	1	3	23294.188	.004
E_2	3	4	2	2	E_2	3	4	1	3	23294.169	.004
E_2	6	5	2	3	E_2	6	5	1	4	22752.801	–.004
E_2	5	5	2	3	E_2	5	5	1	4	22752.831	.000
E_2	4	5	2	3	E_2	4	5	1	4	22752.801	.001
E_2	7	6	2	4	E_2	7	6	1	5	22616.364	–.012
E_2	6	6	2	4	E_2	6	6	1	5	22616.273	–.003
E_2	5	6	2	4	E_2	5	6	1	5	22616.385	–.008
E_2	8	7	2	5	E_2	8	7	1	6	23220.942	–.011
E_2	7	7	2	5	E_2	7	7	1	6	23220.636	–.005
E_2	6	7	2	5	E_2	6	7	1	6	23220.997	–.001
E_3	9	8	2	6	E_3	9	8	1	7	20852.018	.001
E_3	8	8	2	6	E_3	8	8	1	7	20851.156	–.001
E_3	7	8	2	6	E_3	7	8	1	7	20852.128	.003
E_3	3	2	0	2	E_3	2	1	0	1	13454.763	.002
E_3	2	2	0	2	E_3	2	1	0	1	13455.613	.001
E_3	2	2	0	2	E_3	1	1	0	1	13454.947	.001
E_3	1	2	0	2	E_3	1	1	0	1	13453.624	.003
E_3	1	2	0	2	E_3	0	1	0	1	13455.290	.003
E_3	4	3	0	3	E_3	3	2	0	2	19923.018	.002
E_3	3	3	0	3	E_3	3	2	0	2	19924.102	.000
E_3	3	3	0	3	E_3	2	2	0	2	19923.251	.001
E_3	2	3	0	3	E_3	2	2	0	2	19921.787	.003
E_3	2	3	0	3	E_3	1	2	0	2	19923.106	–.002
E_3	5	4	0	4	E_3	4	3	0	3	26122.824	.000
E_3	4	4	0	4	E_3	3	3	0	3	26123.090	–.002
E_3	3	4	0	4	E_3	2	3	0	3	26122.861	.005
E_3	3	2	1	2	E_3	2	1	1	1	12597.885	.004
E_3	2	2	1	2	E_3	2	1	1	1	12599.209	–.001
E_3	2	2	1	2	E_3	1	1	1	1	12598.650	.008
E_3	1	2	1	2	E_3	1	1	1	1	12596.585	.009
E_3	1	2	1	2	E_3	0	1	1	1	12597.994	–.001
E_3	4	3	1	3	E_3	3	2	1	2	18830.176	.002
E_3	3	3	1	3	E_3	3	2	1	2	18831.778	–.001
E_3	3	3	1	3	E_3	2	2	1	2	18830.452	.001
E_3	2	3	1	3	E_3	2	2	1	2	18828.286	.002
E_3	2	3	1	3	E_3	1	2	1	2	18830.351	.000
E_3	5	4	1	4	E_3	4	3	1	3	24997.008	–.002
E_3	4	4	1	4	E_3	3	3	1	3	24997.181	.000
E_3	3	4	1	4	E_3	2	3	1	3	24997.109	–.006
E_3	3	2	1	1	E_3	2	1	1	0	14535.027	–.004
E_3	2	2	1	1	E_3	2	1	1	0	14534.421	.002
E_3	2	2	1	1	E_3	1	1	1	0	14535.649	–.004
E_3	1	2	1	1	E_3	1	1	1	0	14536.600	–.005
E_3	1	2	1	1	E_3	0	1	1	0	14533.522	.001
E_3	4	3	1	2	E_3	3	2	1	1	21730.902	.000
E_3	3	3	1	2	E_3	2	2	1	1	21731.113	–.001
E_3	2	3	1	2	E_3	1	2	1	1	21730.703	.000
E_3	4	3	0	3	E_3	3	2	1	2	14767.755	.002
E_3	3	3	0	3	E_3	3	2	1	2	14768.839	.000
E_3	3	3	0	3	E_3	2	2	1	2	14767.512	.001
E_3	2	3	0	3	E_3	2	2	1	2	14766.047	.002
E_3	2	3	0	3	E_3	1	2	1	2	14768.114	.003
E_3	5	4	0	4	E_3	4	3	1	3	22060.405	.002
E_3	4	4	0	4	E_3	4	3	1	3	22061.755	–.002
E_3	4	4	0	4	E_3	3	3	1	3	22060.153	.001
E_3	3	4	0	4	E_3	3	3	1	3	22058.452	.001
E_3	3	4	0	4	E_3	2	3	1	3	22060.616	–.001
E_3	2	1	1	1	E_3	1	0	0	0	12792.801	.000
E_3	1	1	1	1	E_3	1	0	0	0	12793.362	–.006

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
E_3	0	1	1	1	E_3	1	0	0	0	12791.951	.001
E_3	3	2	1	2	E_3	2	1	0	1	18610.025	.002
E_3	2	2	1	2	E_3	2	1	0	1	18611.352	.001
E_3	1	2	1	2	E_3	2	1	0	1	18609.285	.000
E_3	2	2	1	2	E_3	1	1	0	1	18610.684	–.001
E_3	1	2	1	2	E_3	1	1	0	1	18608.617	–.002
E_3	1	2	1	2	E_3	0	1	0	1	18610.295	.010
E_3	4	3	1	3	E_3	3	2	0	2	23985.438	.001
E_3	3	3	1	3	E_3	3	2	0	2	23987.040	–.002
E_3	3	3	1	3	E_3	2	2	0	2	23986.189	–.001
E_3	2	3	1	3	E_3	2	2	0	2	23984.023	–.001
E_3	2	3	1	3	E_3	1	2	0	2	23985.354	.006
E_3	2	1	1	0	E_3	1	0	0	0	13771.485	.012
E_3	1	1	1	0	E_3	1	0	0	0	13770.252	.012
E_3	4	3	2	2	E_3	3	2	2	1	20400.191	–.003
E_3	3	3	2	2	E_3	3	2	2	1	20400.175	–.006
E_3	3	3	2	2	E_3	2	2	2	1	20400.930	–.005
E_3	2	3	2	2	E_3	1	2	2	1	20399.779	–.001
E_3	4	3	2	1	E_3	3	2	2	0	20721.452	.007
E_3	3	3	2	1	E_3	2	2	2	0	20721.935	.009
E_3	2	3	2	1	E_3	1	2	2	0	20721.119	.008
E_3	5	4	1	3	E_3	5	4	0	4	12583.443	–.003
E_3	4	4	1	3	E_3	5	4	0	4	12583.185	–.010
E_3	5	4	1	3	E_3	4	4	0	4	12582.086	–.007
E_3	4	4	1	3	E_3	4	4	0	4	12581.845	.004
E_3	3	4	1	3	E_3	4	4	0	4	12582.164	.007
E_3	4	4	1	3	E_3	3	4	0	4	12583.547	.004
E_3	3	4	1	3	E_3	3	4	0	4	12583.856	–.003
E_3	6	5	1	4	E_3	6	5	0	5	16292.416	.001
E_3	5	5	1	4	E_3	5	5	0	5	16290.701	.002
E_3	4	5	1	4	E_3	4	5	0	5	16292.762	–.001
E_3	7	6	1	5	E_3	7	6	0	6	20965.334	.001
E_3	6	6	1	5	E_3	6	6	0	6	20963.575	.003
E_3	5	6	1	5	E_3	5	6	0	6	20965.630	.000
E_3	8	7	1	6	E_3	8	7	0	7	26397.188	.002
E_3	7	7	1	6	E_3	7	7	0	7	26395.465	.004
E_3	6	7	1	6	E_3	6	7	0	7	26397.423	–.012
E_3	3	2	2	1	E_3	3	2	1	2	20876.168	.003
E_3	2	2	2	1	E_3	3	2	1	2	20875.412	.002
E_3	3	2	2	1	E_3	2	2	1	2	20874.842	.006
E_3	2	2	2	1	E_3	2	2	1	2	20874.086	.004
E_3	1	2	2	1	E_3	2	2	1	2	20875.255	.001
E_3	2	2	2	1	E_3	1	2	1	2	20876.146	–.002
E_3	1	2	2	1	E_3	1	2	1	2	20877.322	.001
E_3	4	3	2	2	E_3	4	3	1	3	22446.185	.001
E_3	3	3	2	2	E_3	3	3	1	3	22444.566	.000
E_3	2	3	2	2	E_3	3	3	1	3	22444.585	.001
E_3	3	3	2	2	E_3	2	3	1	3	22446.730	–.003
E_3	2	3	2	2	E_3	2	3	1	3	22446.748	–.002
E_3	5	4	2	3	E_3	5	4	1	4	24511.073	.000
E_3	4	4	2	3	E_3	4	4	1	4	24509.633	.001
E_3	4	4	2	3	E_3	3	4	1	4	24511.864	.000
E_3	3	4	2	3	E_3	3	4	1	4	24511.442	–.001
E_3	3	2	2	0	E_3	3	2	1	1	18216.032	–.002
E_3	2	2	2	0	E_3	3	2	1	1	18215.219	–.001
E_3	3	2	2	0	E_3	2	2	1	1	18216.644	–.002
E_3	2	2	2	0	E_3	2	2	1	1	18215.827	–.006
E_3	1	2	2	0	E_3	2	2	1	1	18217.090	–.008
E_3	2	2	2	0	E_3	1	2	1	1	18214.874	–.006
E_3	1	2	2	0	E_3	1	2	1	1	18216.138	–.008
E_3	4	3	2	1	E_3	4	3	1	2	17206.587	.010
E_3	3	3	2	1	E_3	4	3	1	2	17206.248	.005
E_3	4	3	2	1	E_3	3	3	1	2	17206.984	.006
E_3	3	3	2	1	E_3	3	3	1	2	17206.645	.001

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	$\text{o} - \text{c}$
E_3	2	3	2	1	E_3	3	3	1	2	17207.097	.003
E_3	3	3	2	1	E_3	2	3	1	2	17206.104	.001
E_3	2	3	2	1	E_3	2	3	1	2	17206.552	-.001
E_3	5	4	2	2	E_3	5	4	1	3	16420.982	.001
E_3	4	4	2	2	E_3	4	4	1	3	16420.982	.007
E_3	3	4	2	2	E_3	3	4	1	3	16420.982	.000
E_3	6	5	2	3	E_3	6	5	1	4	16159.468	-.001
E_3	5	5	2	3	E_3	5	5	1	4	16159.275	.001
E_3	4	5	2	3	E_3	4	5	1	4	16159.511	.002
E_3	7	6	2	4	E_3	7	6	1	5	16686.279	-.002
E_3	6	6	2	4	E_3	6	6	1	5	16685.855	-.004
E_3	5	6	2	4	E_3	5	6	1	5	16686.345	-.007
E_3	8	7	2	5	E_3	8	7	1	6	18202.930	-.003
E_3	7	7	2	5	E_3	7	7	1	6	18202.281	-.003
E_3	6	7	2	5	E_3	6	7	1	6	18203.030	.003
E_3	5	4	1	3	E_3	4	3	2	2	12197.667	.002
E_3	3	4	1	3	E_3	4	3	2	2	12197.733	.003
E_3	4	4	1	3	E_3	3	3	2	2	12197.429	.002
E_3	3	4	1	3	E_3	3	3	2	2	12197.733	-.010
E_3	3	4	1	3	E_3	2	3	2	2	12197.712	-.013
E_3	6	5	1	4	E_3	5	4	2	3	20913.071	.002
E_3	5	5	1	4	E_3	4	4	2	3	20912.638	.002
E_3	4	5	1	4	E_3	3	4	2	3	20913.176	.001
E_3	3	2	2	1	E_3	3	2	1	1	17960.342	.000
E_3	2	2	2	1	E_3	3	2	1	1	17959.586	-.002
E_3	3	2	2	1	E_3	2	2	1	1	17960.954	.000
E_3	2	2	2	1	E_3	2	2	1	1	17960.190	-.010
E_3	1	2	2	1	E_3	2	2	1	1	17961.364	-.009
E_3	2	2	2	1	E_3	1	2	1	1	17959.244	-.004
E_3	1	2	2	1	E_3	1	2	1	1	17960.408	-.013
E_3	3	2	2	0	E_3	3	2	1	2	21131.857	.001
E_3	2	2	2	0	E_3	3	2	1	2	21131.043	.000
E_3	3	2	2	0	E_3	2	2	1	2	21130.532	.004
E_3	2	2	2	0	E_3	2	2	1	2	21129.717	.003
E_3	1	2	2	0	E_3	2	2	1	2	21130.980	.001
E_3	1	2	2	0	E_3	1	2	1	2	21133.047	.001
E_3	4	3	2	2	E_3	4	3	1	2	16629.633	.000
E_3	3	3	2	2	E_3	3	3	1	2	16630.019	-.002
E_3	2	3	2	2	E_3	2	3	1	2	16629.490	-.008
E_3	4	3	2	1	E_3	4	3	1	3	23023.134	.007
E_3	3	3	2	1	E_3	3	3	1	3	23021.196	.007
E_3	2	3	2	1	E_3	2	3	1	3	23023.811	.005
E_4	6	5	2	4	E_4	6	5	1	5	22716.303	-.001
E_4	5	5	2	4	E_4	5	5	1	5	22714.754	-.002
E_4	4	5	2	4	E_4	4	5	1	5	22716.623	.003
E_4	6	5	1	4	E_4	6	5	0	5	18380.815	-.002
E_4	5	5	1	4	E_4	5	5	0	5	18379.630	-.001
E_4	4	5	1	4	E_4	4	5	0	5	18381.053	-.006
E_4	7	6	1	5	E_4	7	6	0	6	21718.808	-.005
E_4	6	6	1	5	E_4	6	6	0	6	21717.357	-.004
E_4	5	6	1	5	E_4	5	6	0	6	21719.054	-.004
E_4	8	7	1	6	E_4	8	7	0	7	26195.475	-.003
E_4	7	7	1	6	E_4	7	7	0	7	26193.864	-.004
E_4	6	7	1	6	E_4	6	7	0	7	26195.727	.017
E_4	6	5	2	3	E_4	6	5	1	4	24364.962	.003
E_4	5	5	2	3	E_4	5	5	1	4	24364.591	.001
E_4	4	5	2	3	E_4	4	5	1	4	24365.027	-.007
E_4	7	6	2	4	E_4	7	6	1	5	24947.000	-.004
E_4	6	6	2	4	E_4	6	6	1	5	24946.733	.001
E_4	5	6	2	4	E_4	5	6	1	5	24947.060	.010
E_4	8	7	2	5	E_4	8	7	1	6	25703.291	.000
E_4	7	7	2	5	E_4	7	7	1	6	25703.037	-.002
E_4	3	2	0	2	E_4	2	1	0	1	12820.343	.001
E_4	2	2	0	2	E_4	2	1	0	1	12820.757	.001

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	$\text{o} - \text{c}$
E_4	2	2	0	2	E_4	1	1	0	1	12820.928	.000
E_4	1	2	0	2	E_4	0	1	0	1	12819.852	-.001
E_4	4	3	0	3	E_4	3	2	0	2	19485.377	.002
E_4	3	3	0	3	E_4	3	2	0	2	19486.097	.001
E_4	3	3	0	3	E_4	2	2	0	2	19485.683	.001
E_4	2	3	0	3	E_4	2	2	0	2	19484.708	.000
E_4	2	3	0	3	E_4	1	2	0	2	19485.349	-.003
E_4	5	4	0	4	E_4	4	3	0	3	25924.789	.004
E_4	4	4	0	4	E_4	3	3	0	3	25925.098	-.001
E_4	3	4	0	4	E_4	2	3	0	3	25924.774	.003
E_4	3	2	1	2	E_4	2	1	1	1	13593.183	.000
E_4	2	2	1	2	E_4	1	1	1	1	13593.622	-.002
E_4	4	3	1	3	E_4	3	2	1	2	19538.608	.000
E_4	3	3	1	3	E_4	3	2	1	2	19539.966	.000
E_4	3	3	1	3	E_4	2	2	1	2	19538.956	.000
E_4	2	3	1	3	E_4	2	2	1	2	19537.122	.000
E_4	2	3	1	3	E_4	1	2	1	2	19538.691	-.002
E_4	5	4	1	4	E_4	4	3	1	3	25385.768	.000
E_4	4	4	1	4	E_4	3	3	1	3	25386.017	.000
E_4	3	4	1	4	E_4	2	3	1	3	25385.827	-.003
E_4	4	3	1	2	E_4	3	2	1	1	20832.341	.001
E_4	3	3	1	2	E_4	2	2	1	1	20832.980	.000
E_4	2	3	1	2	E_4	1	2	1	1	20831.954	.004
E_4	2	1	1	0	E_4	2	1	1	1	14241.235	-.004
E_4	1	1	1	0	E_4	2	1	1	1	14240.838	-.004
E_4	2	1	1	0	E_4	1	1	1	1	14240.669	-.001
E_4	1	1	1	0	E_4	1	1	1	1	14240.272	-.001
E_4	0	1	1	0	E_4	1	1	1	1	14241.271	.006
E_4	1	1	1	0	E_4	0	1	1	1	14241.695	-.001
E_4	4	3	1	2	E_4	4	3	1	3	10939.307	.001
E_4	3	3	1	2	E_4	3	3	1	3	10937.780	.003
E_4	2	3	1	2	E_4	2	3	1	3	10939.841	.000
E_4	3	2	1	2	E_4	2	1	0	1	16245.438	.003
E_4	2	2	1	2	E_4	2	1	0	1	16246.447	.001
E_4	2	2	1	2	E_4	1	1	0	1	16246.620	.002
E_4	1	2	1	2	E_4	1	1	0	1	16245.050	.003
E_4	1	2	1	2	E_4	0	1	0	1	16244.617	.001
E_4	4	3	1	3	E_4	3	2	0	2	22963.701	.000
E_4	3	3	1	3	E_4	3	2	0	2	22965.058	-.002
E_4	3	3	1	3	E_4	2	2	0	2	22964.646	.000
E_4	2	3	1	3	E_4	2	2	0	2	22962.812	.000
E_4	2	3	1	3	E_4	1	2	0	2	22963.456	.000
E_4	2	1	1	0	E_4	2	1	0	1	16893.493	.002
E_4	1	1	1	0	E_4	2	1	0	1	16893.095	.000
E_4	2	1	1	0	E_4	1	1	0	1	16893.665	.001
E_4	1	1	1	0	E_4	1	1	0	1	16893.268	.001
E_4	0	1	1	0	E_4	1	1	0	1	16894.260	.001
E_4	1	1	1	0	E_4	0	1	0	1	16892.836	.000
E_4	3	2	1	1	E_4	3	2	0	2	13070.663	-.004
E_4	2	2	1	1	E_4	3	2	0	2	13069.858	.000
E_4	3	2	1	1	E_4	2	2	0	2	13070.251	-.002
E_4	2	2	1	1	E_4	2	2	0	2	13069.445	.001
E_4	2	2	1	1	E_4	1	2	0	2	13070.089	.001
E_4	1	2	1	1	E_4	1	2	0	2	13071.338	-.009
E_4	4	3	1	2	E_4	4	3	0	3	14417.632	.000
E_4	3	3	1	2	E_4	3	3	0	3	14416.743	.002
E_4	2	3	1	2	E_4	2	3	0	3	14417.943	-.001
E_4	5	4	1	3	E_4	5	4	0	4	16081.489	-.001
E_4	4	4	1	3	E_4	4	4	0	4	16080.553	-.001
E_4	3	4	1	3	E_4	3	4	0	4	16081.730	-.001
E_4	2	1	1	0	E_4	1	0	0	0	21471.265	-.001
E_4	1	1	1	0	E_4	1	0	0	0	21470.869	-.001
E_4	0	1	1	0	E_4	1	0	0	0	21471.860	-.001
E_4	3	2	1	1	E_4	2	1	0	1	25891.010	.001

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
E_4	2	2	1	1	E_4	2	1	0	1	25890.208	.008
E_4	2	2	1	1	E_4	1	1	0	1	25890.375	.003
E_4	1	2	1	1	E_4	1	1	0	1	25891.632	.001
E_4	1	2	1	1	E_4	0	1	0	1	25891.210	.010
E_4	3	2	0	2	E_4	2	1	1	1	10168.090	.001
E_4	2	2	0	2	E_4	2	1	1	1	10168.497	–.006
E_4	2	2	0	2	E_4	1	1	1	1	10167.928	–.006
E_4	1	2	0	2	E_4	1	1	1	1	10167.291	.001
E_4	1	2	0	2	E_4	0	1	1	1	10168.712	–.001
E_4	4	3	0	3	E_4	3	2	1	2	16060.278	–.003
E_4	3	3	0	3	E_4	3	2	1	2	16060.999	–.003
E_4	3	3	0	3	E_4	2	2	1	2	16059.991	–.001
E_4	2	3	0	3	E_4	2	2	1	2	16059.017	–.002
E_4	2	3	0	3	E_4	1	2	1	2	16060.594	.004
E_4	5	4	0	4	E_4	4	3	1	3	22446.463	.004
E_4	4	4	0	4	E_4	4	3	1	3	22447.491	–.002
E_4	3	4	0	4	E_4	3	3	1	3	22444.835	.001
E_4	3	4	0	4	E_4	2	3	1	3	22446.676	.008
E_4	4	3	2	2	E_4	3	2	2	1	20952.056	–.002
E_4	3	3	2	2	E_4	2	2	2	1	20952.056	–.010
E_4	2	3	2	2	E_4	1	2	2	1	20952.087	.002
E_4	3	2	2	1	E_4	3	2	1	2	14439.555	.001
E_4	2	2	2	1	E_4	3	2	1	2	14439.703	–.003
E_4	3	2	2	1	E_4	2	2	1	2	14438.544	.001
E_4	2	2	2	1	E_4	2	2	1	2	14438.696	.001
E_4	1	2	2	1	E_4	2	2	1	2	14438.460	.001
E_4	2	2	2	1	E_4	1	2	1	2	14440.267	.000
E_4	1	2	2	1	E_4	1	2	1	2	14440.031	.000
E_4	3	2	2	1	E_4	2	1	1	0	13791.497	–.001
E_4	2	2	2	1	E_4	2	1	1	0	13791.651	.001
E_4	2	2	2	1	E_4	1	1	1	0	13792.045	–.001
E_4	1	2	2	1	E_4	1	1	1	0	13791.807	–.003
E_4	1	2	2	1	E_4	0	1	1	0	13790.820	.002
E_4	4	3	2	2	E_4	4	3	1	3	15853.003	.000
E_4	3	3	2	2	E_4	4	3	1	3	15853.165	.001
E_4	4	3	2	2	E_4	3	3	1	3	15851.647	.003
E_4	3	3	2	2	E_4	3	3	1	3	15851.807	.002
E_4	2	3	2	2	E_4	3	3	1	3	15851.593	.005
E_4	3	3	2	2	E_4	2	3	1	3	15853.640	.001
E_4	2	3	2	2	E_4	2	3	1	3	15853.425	.003
E_4	4	3	2	2	E_4	3	2	1	1	25746.040	.003
E_4	3	3	2	2	E_4	2	2	1	1	25747.008	.000
E_4	4	3	2	1	E_4	4	3	1	2	24028.081	–.004
E_4	3	3	2	1	E_4	3	3	1	2	24027.270	–.003
E_4	2	3	2	1	E_4	2	3	1	2	24028.360	–.009
E_4	5	4	2	2	E_4	5	4	1	3	24028.888	–.003
E_4	3	4	2	2	E_4	3	4	1	3	24029.031	.004
E_4	5	4	1	3	E_4	4	3	2	2	22674.944	–.002
E_4	4	4	1	3	E_4	3	3	2	2	22674.885	.002
E_4	3	4	1	3	E_4	2	3	2	2	22674.979	.002
E_4	4	3	2	2	E_4	4	3	0	3	19331.328	–.002
E_4	3	3	2	2	E_4	3	3	0	3	19330.771	.001
E_4	2	3	2	2	E_4	2	3	0	3	19331.526	.000
E_4	4	3	2	1	E_4	4	3	2	2	19114.381	–.006
E_4	3	3	2	1	E_4	3	3	2	2	19113.249	.004
E_4	2	3	2	1	E_4	2	3	2	2	19114.795	.008
E_4	5	4	2	2	E_4	5	4	2	3	18451.952	–.003
E_4	4	4	2	2	E_4	4	4	2	3	18451.387	.000
E_4	3	4	2	2	E_4	3	4	2	3	18452.109	.008
E_4	4	3	1	2	E_4	3	2	2	1	16038.361	.001
E_4	3	3	1	2	E_4	2	2	2	1	16038.038	.000
E_4	2	3	1	2	E_4	1	2	2	1	16038.505	.001
E_4	3	2	1	1	E_4	2	1	1	1	23238.755	–.001
E_4	2	2	1	1	E_4	2	1	1	1	23237.947	.000

Table 4 (continued)

Γ'	F'	J'	K'_a	K'_c	Γ''	F''	J''	K''_a	K''_c	Observed	o – c
E_4	2	2	1	1	E_4	1	1	1	1	23237.377	–.001
E_4	1	2	1	1	E_4	1	1	1	1	23238.631	–.006
E_4	1	2	1	1	E_4	0	1	1	1	23240.058	–.001
E_4	5	4	1	4	E_4	4	3	1	2	14446.460	–.002
E_4	4	4	1	4	E_4	3	3	1	2	14448.237	–.003
E_4	3	4	1	4	E_4	2	3	1	2	14445.988	–.001
E_4	5	4	2	3	E_4	5	4	1	4	18719.117	.000
E_4	4	4	2	3	E_4	4	4	1	4	18717.646	.001
E_4	3	4	2	3	E_4	3	4	1	4	18719.494	–.002

^a The symbols Γ , F , J , K_a , K_c represent the symmetry species from Table 1, the total angular momentum including the nitrogen nuclear spin, and the usual asymmetric top rotational quantum numbers, respectively.

^b The observed transition frequencies and the observed-minus-calculated (o – c) residuals are all in MHz. The standard uncertainty (type B, $k = 1$) in the observed frequencies is 0.004 MHz.

^c The 48 parameters used in the Hamiltonian of Eq. (6), as determined from a least-squares fit of the 839 hyperfine components listed above (which involve 216 torsion–rotation transitions and 152 torsion–rotation energy levels) are given in Table 3. The root-mean-square deviation of the fit is 3.84 kHz.

$$\begin{bmatrix} A' & 0 \\ 0 & B' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} A_{aa} & A_{ab} \\ A_{ab} & A_{bb} \end{bmatrix} \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix},$$

$$\begin{aligned} q_1 &= -2F_1(\rho_{1a}\cos\theta - \rho_{1b}\sin\theta) - 2F_{12}(\rho_{2a}\cos\theta - \rho_{2b}\sin\theta), \\ r_1 &= -2F_1(\rho_{1a}\sin\theta + \rho_{1b}\cos\theta) - 2F_{12}(\rho_{2a}\sin\theta + \rho_{2b}\cos\theta), \\ q_2 &= -2F_2(\rho_{2a}\cos\theta - \rho_{2b}\sin\theta) - 2F_{12}(\rho_{1a}\cos\theta - \rho_{1b}\sin\theta), \\ r_2 &= -2F_2(\rho_{2a}\sin\theta + \rho_{2b}\cos\theta) - 2F_{12}(\rho_{1a}\sin\theta + \rho_{1b}\cos\theta), \end{aligned} \quad (11)$$

with

$$\begin{aligned} A_{aa} &= A + F_1\rho_{1a}^2 + F_2\rho_{2a}^2 + 2F_{12}\rho_{1a}\rho_{2a}, \\ A_{ab} &= F_1\rho_{1a}\rho_{1b} + F_2\rho_{2a}\rho_{2b} + F_{12}(\rho_{1a}\rho_{2b} + \rho_{2a}\rho_{1b}), \\ A_{bb} &= B + F_1\rho_{1b}^2 + F_2\rho_{2b}^2 + 2F_{12}\rho_{1b}\rho_{2b}. \end{aligned} \quad (12)$$

The quantities on the left of Eqs. (11) were determined in our fit and are given in Table 3. From the point of view of the PAM quantities on the right, and taking into account Eqs. (10) and (12), Eqs. (11) represent seven equations in the seven unknowns: A , B , ρ_{1a} , ρ_{1b} , ρ_{2a} , ρ_{2b} , and θ . Values for the seven PAM quantities obtained by solving these non-linear equations are given in the top part of Table 5.

The six quantities represented by the direction cosines $\lambda_{1\beta}$ and $\lambda_{2\beta}$ of the axes of top 1 and 2, and the moments of inertia I_1 and I_2 of top 1 and 2 can be determined from the four equations represented by (8c) and (8d), together with the sums $\lambda_{1a}^2 + \lambda_{1b}^2 = \lambda_{2a}^2 + \lambda_{2b}^2 = 1$. Values for these six quantities are given in the lower part of Table 5.

A consistency check is now possible, since the quantities

$$\begin{aligned} F_1 &= (h/8\pi^2c)R_2/(R_1R_2 - Q^2)I_1, \\ F_2 &= (h/8\pi^2c)R_1/(R_1R_2 - Q^2)I_2, \\ F_{12} &= -(h/8\pi^2c)Q/(R_1R_2 - Q^2)(I_1I_2)^{1/2}, \end{aligned} \quad (13)$$

Table 5

Molecular parameters^a in the PAM system derived from the fitting parameters in Table 3, using Eqs. (8)–(12)^b

<i>A</i>	10162(2) MHz	θ	−0.02722(4) rad	ρ_{2a}	0.05696(5)
<i>B</i>	3885.04(4) MHz	ρ_{1a}	0.0525(1)	ρ_{2b}	0.01122(1)
<i>C</i>	2902.736(5) MHz	ρ_{1b}	0.00895(2)		
<hr/>					
<i>I</i> ₁	2.858(6) u Å ²	λ_{1a}	0.9133(3)	λ_{2a}	0.8889(1)
<i>I</i> ₂	3.187(3) u Å ²	λ_{1b}	0.4072(7)	λ_{2b}	0.4581(2)

^a Numbers in parentheses are type-*B* uncertainties ($k = 1$) estimated from the type-*A* uncertainties ($k = 1$) of the fitting parameters in Table 3.

^b The eight parameters above the dotted line were determined from Eqs. (10)–(12) and various fitting parameters in Table 3. The six parameters below the dotted line were determined from parameters above the line and Eqs. (8c) and (8d).

where the units of the F 's are $length^{-1}$, the units of the I 's are $mass \times length^2$, and where

$$\begin{aligned} R_1 &= 1 - \sum_{\beta} \rho_{1\beta} \lambda_{1\beta}, \\ R_2 &= 1 - \sum_{\beta} \rho_{2\beta} \lambda_{2\beta}, \\ Q &= -\sum_{\beta} \lambda_{1\beta} \lambda_{2\beta} (I_1 I_2)^{1/2} / I_{\beta}, \end{aligned} \quad (14)$$

can be calculated from various parameters in Table 5. These calculated F 's can then be compared with F values determined directly by the fitting procedure. (Note, however, that F values from the fit were also needed in Eqs. (11) and (12) to obtain the parameters in Table 5.) The values calculated from Eqs. (13) of $F_1 = 6.239 \text{ cm}^{-1}$, $F_2 = 5.621 \text{ cm}^{-1}$, and $F_{12} = 0.335 \text{ cm}^{-1}$ are larger than the corresponding fitted F 's by 6, 2, and 5%, respectively. These relatively small inconsistencies probably arise from the failure to consider vibrational averaging effects. In particular, the planar peptide linkage may itself undergo noticeable out-of-plane distortion whenever an internally rotated methyl group destroys the local plane of symmetry at either end of the molecule.

6.2. Inertial defect

The PAM rotational constants A , B and C (not A' , B') obtained above produce a value of $-5.713(10) \text{ u Å}^2$ for the inertial defect $\Delta \equiv I_{cc} - I_{aa} - I_{bb}$. For the inertial defect of *N*-methylacetamide with a planar skeleton, we have the relation

$$\Delta = -2\sum_n m_n r_{nc}^2 + \Delta_{\text{vib}}, \quad (15)$$

where m_n and r_{nc} are the mass and distance from the *ab* plane of the n th atom, and Δ_{vib} denotes the vibrational contribution [26] to the inertial defect of the planar skeleton (the electronic and centrifugal distortion contributions are neglected). By using a relation based on the assumption that the C_3 symmetry of each of the two methyl tops is maintained during internal rotation

$$2\sum_n m_n r_{nc}^2 = I_1 + I_2, \quad (16)$$

we find $\Delta_{\text{vib}} = +0.332(19) \text{ u Å}^2$ from $I_1 + I_2 = 6.045(9) \text{ u Å}^2$. Such a positive value for Δ_{vib} suggests that con-

tributions from in-plane low-frequency modes are larger than the contributions from out-of-plane low-frequency modes in this molecule, though a careful quantitative treatment would be necessary to confirm this interpretation.

6.3. Barrier heights to internal rotation of the methyl tops

As an important result of the present study, barrier heights to internal rotation motion of methyl tops 1 and 2 were determined to be $V_{3,1} = 79.062(93) \text{ cm}^{-1}$ and $V_{3,2} = 73.468(51) \text{ cm}^{-1}$ as shown in Table 3. These values for the barrier heights of the two methyl tops are close to those of peptide molecules studied recently by other groups, e.g., $80.06487(14) \text{ cm}^{-1}$ for N-CH_3 of *N*-methylpropionamide [27], and $98.4(2)$ and $84.0(3) \text{ cm}^{-1}$ for the acetyl and amide methyl groups, respectively, of *N*-acetyl-alanine-*N'*-methylamide [28].

The methyl-group internal rotation angles in *N*-methylacetamide correspond exactly to the Ramachandran angles usually used to describe internal rotation about the C_{α} carbon bonds in polypeptides [29], since we can make the identifications $\text{H}_3\text{C}_{\alpha}-(\psi)-\text{C}(=\text{O})-\text{NH}-(\phi)-\text{C}_{\alpha}\text{H}_3$. It is difficult to assign from only chemical intuition the two barrier heights determined in the global fit to those for C-CH_3 and N-CH_3 , since the two values are very close to each other. A more objective approach involves comparing the direction cosines $\lambda_{a\text{-top}}$ between each top axis and the *a*-axis obtained from the global fit with those calculated from the structural parameters given in the ab initio study of Cuevas et al. [1]. It is rather clear from the comparison shown in Table 6 that top 1 and top 2 correspond to the $\text{N}-(\phi)-\text{CH}_3$ and the $\text{C}-(\psi)-\text{CH}_3$ rotors, respectively. Table 6 also shows that the observed spectrum is from the *trans* conformer of the molecule, which was found to be more stable than the *cis* form in the ab initio study [1]. We note that these internal-rotation barriers are both about $0.3 \text{ kT}_{\text{biosystems}}$, i.e., about 1/3 of the thermal energy available in biosystems, which is consistent with the observation that biosystems can easily explore a variety of Ramachandran angle distributions in an attempt to find the lowest-energy folded conformation.

Table 6

Comparison of values from the present study with ab initio values for the direction cosine between each top axis and the principal *a*-axis of the molecule

This work			Ab initio ^a	
			<i>trans</i>	<i>cis</i>
λ_{1a}	0.9133(3)	$\lambda_{a\text{-NC}}$	0.9161	0.8841
λ_{2a}	0.8889(1)	$\lambda_{a\text{-CC}}$	0.8590	0.0286

^a Direction cosines calculated from the B3LYP structures in Tables 1 and 2 of [1].

6.4. Top–top interactions

Interaction between the two methyl tops in the kinetic energy part of the Hamiltonian is given (to lowest order) by the constant F_{12} in Eqs. (13). A qualitative feeling for this interaction can be obtained by examining the limit in which the two tops are structurally identical ($I_1 = I_2 \equiv I_{\text{top}}$) and the molecule is an accidental spherical top ($I_a = I_b = I_c \equiv I_{\text{mol}}$). Eqs. (14) then yield $R_1 = R_2 = 1 - I_{\text{top}}/I_{\text{mol}} = 1 - \rho$ and $Q = -\rho\lambda_1 \cdot \lambda_2$. These values give $F_{12}/F_1 = F_{12}/F_2 \approx -\rho_1 = -\rho_2$, since the two top-axis directions are nearly parallel. With values from Tables 3 and 5, this equation averages to $0.056(2) \approx 0.056(2)$. The fact that the top–top kinetic coupling is proportional to ρ can be understood physically by noting that a sphere with an infinite moment of inertia cannot sense the rotation of two very light tops attached to it, and therefore cannot transmit kinetic information (cannot kinetically couple) one top to the other. A slightly more sophisticated version of this argument would note that, if atomic displacements for an infinitesimal methyl-group internal rotation are to be orthogonal to atomic displacements for any infinitesimal overall rotation (which is required by the Eckart condition for zeroth-order separation of torsion and overall rotation), then a rotation of either top through an angle α requires a backward rotation of the frame through an angle $-\rho\alpha$, and it is this backward rotation of the frame that transmits kinetic information from one top to the other, as long as the two top axes are not mutually perpendicular. As $\rho \rightarrow 0$, the amount of kinetic information transferred also goes to zero. (This argument is the rotational analog of the translational argument used to understand the small kinetic coupling between the two A–B stretching motions in an AB_2 molecule with a massive A and light B atoms.)

Interaction between the two tops in the potential energy part of the Hamiltonian is given (to lowest order) by the constants V_{12c} and V_{12s} in Table 3. Since the two methyl tops in *N*-methylacetamide are quite far separated from each other spatially, we do not expect direct steric interactions between them. Rather, we presume that these top–top couplings, which fall in the range of 1–4% of the individual-top internal-rotation barriers, represent top–top potential-energy interactions transmitted directly through the chemical bonds via subtle changes in their various properties (direction, length, electron distribution, etc.).

The fact that all top–top coupling is small in this molecule makes it possible to view the system in zeroth order as two non-interacting light tops connected to a heavy frame, which we believe contributes to the simple

sum and difference regularities described for the separate-symmetry-species fits in Section 4.

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