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A flexible method for calculating vibrational spectra of clusters applied to methanol

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Abstract. A method is presented for calculating vibrational spectra of clusters using intra- and intermolecular potential models of different origin. The two types of potentials are tuned and coupled to construct a total cluster potential. The determination of minima on this cluster potential energy surface, and the expansion of the potential about the minimum configurations makes it possible to apply standard spectroscopic methods. Starting from a normal mode analysis, harmonic and anharmonic frequency shifts are calculated using perturbational and variational methods for methanol clusters from the dimer to the hexamer. The results using the empirical OPLS potential model are compared with each other, with the harmonic line shift calculations for a calculated potential in the SCF approximation, and with the experimental data. There is an improvement with respect to the results obtained so far, however, the need for a better description of the intermolecular potential is pointed out.

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1 Introduction

The investigation of atomic and molecular clusters has attracted much interest in recent years. One of reasons is that more and more experimental and theoretical tools have been developed that allow us to ask and to get answered questions about the nature of cluster properties. One of the most basic questions concerns the structure of clusters, since it gives detailed information on the Potential Energy Surface (PES) of the cluster constituents. Spectroscopy is one of the most popular means to determine the cluster structure. Many difficulties, however, have to be overcome to get the desired data. A crucial problem is the production of neutral clusters of a single size. Buck and Meyer used the momentum transfer in a scattering experiment to select the cluster size [1]. Subsequently the selected cluster beam interacts with intense infrared radiation of the frequency ν which leads to predissociation. The dissociated fraction is then determined as a function of the frequency ν [2–5].

These experiments provide the main motivation for the present study, that is to say, we want to investigate the infrared spectrum of a cluster of well-defined size. In our approach we assume that the experimental rotational-vibrational spectra are still determined by fundamental vibrational excitations of the energetically most stable structures. Since rotational transitions are not resolved in these experiments, we are only interested in pure vibrational spectra that may include effects of the rotational movement on the vibrational energy levels.

To calculate the vibrational spectrum of a cluster, a PES is needed that includes intramolecular as well as intermolecular interactions of the cluster constituents. Accurate, complete *ab initio* force fields are usually still too expensive to map all areas of the PES which we are interested in. Accurate intramolecular force fields, however, are available for many molecules as well as potentials that describe their intermolecular interactions. Since intramolecular modes are excited in the experiments described above we need to know about the influence of the intermolecular interaction on the intramolecular modes, *i.e.* we are interested in line shifts of intramolecular modes with respect to their monomer gas phase values.

There are several approaches available which are based on monomer properties. Buck and Schmidt [6] extended the idea of Buckingham [7] and treated the intermolecular interaction as an additional perturbation along with anharmonic intramolecular terms for clusters of identical molecules. Beu removed some simplifications that were assumed in reference [6] which yields different and quite complicated formulae in second order perturbation theory [8]. A further generalization of the method was developed by Beu and Takeuchi [9] that includes the treatment of degenerate intramolecular modes. Since all these approaches start with uncoupled molecular Hamiltonians in zeroth order perturbation theory, we call them comprisingly the *molecular approach* (M).

Here, we follow a different approach that was used already by Reimers and Watts to calculate the structure and vibrational spectra of small water clusters without giving explicit formulae for the cluster potential [10]. Again we start using decoupled intra- and intermolecular model potentials. These potentials serve as input to construct a complete cluster potential making thus available the whole set of standard spectroscopical methods. Consequently we call it the *cluster approach* (C). In Section 2 we give a more rigorous formulation of the basic ideas concerning the construction of the total cluster PES using intramolecular force fields and analytical intermolecular potentials. In Section 3 we describe the standard methods to calculate the harmonic and anharmonic vibrational energy levels of a given cluster. In Section 4 we present results for methanol clusters from the dimer to the hexamer and compare them with experimental data and calculations in the Self-Consistent-Field (SCF) approximation [11]. In Section 5 we finish with a discussion of our results.

2 The cluster Potential Energy Surface (PES)

In this section we want to describe how to combine optimized intra- and intermolecular interaction potentials with each other. Since the ideal situation of potentials which are tuned to each other will be rather rare, we elaborate on some further approximations.

2.1 Intramolecular potential

Usually the intramolecular potential is calculated in the adiabatic Born-Oppenheimer approximation. The electronic Schrödinger equation is solved for a given configuration of the atomic nuclei. Calculating the electronic energy eigenvalues on a grid around the minimum configuration of a molecule yields an *ab initio* PES. It is used to determine the vibrational energy levels of the molecule. Typically the intramolecular potential is expanded in a series around the minimum configuration using internal coordinates.

$$V^{\mathrm{intra}}=V_0+\frac{1}{2}\sum_{i,j=1}^{3N-6} f_{ij}(\mathrm{R}_i-\mathrm{R}_i^0)(\mathrm{R}_j-\mathrm{R}_j^0)+\ \dots\ , \qquad (1)$$

where V_0 is the binding energy of the molecule (V_0 is of no importance in the further discussion and arbitrarily set to zero), f_{ij} are quadratic force constants with respect to the internal coordinates R_i, R_i^0 denotes the components of the minimum configuration $\mathbf{R}_0=(\mathrm{R}_1^0,\dots,\mathrm{R}_{3N-6}^0)$, and N is the number of atomic nuclei in the molecule. The $3N-6$ internal coordinates are given as analytical functions of the $3N$ Cartesian coordinates

$$\mathrm{R}_i=R_i(x_1,\dots,x_{3N};\mathbf{R}^0),\quad i=1,\dots,3N-6. \qquad (2)$$

In general, the coordinate transformation between internal and Cartesian coordinates is nonlinear. Usually the transformation is performed using so-called $\underline{\underline{B}}$-tensors. However, we simply use the analytical expressions connecting internal and Cartesian coordinates. The intramolecular interaction for M molecules is given by

$$\begin{aligned}V^{\mathrm{intra}}=\sum_{m}^{M}\Bigg(&\frac{1}{2}\sum_{i,j}^{3N_m-6} f_{ij}^{m}R_i^m(x_{1m},\dots,x_{3N_m};\mathbf{R}_0^m)\\ &\times R_j^m(x_{1m},\dots,x_{3N_m};\mathbf{R}_0^m)\\ &+\frac{1}{6}\sum_{i,j,k}^{3N_m-6} f_{ijk}^{m}R_i^m(x_{1m},\dots,x_{3N_m};\mathbf{R}_0^m)\\ &\times R_j^m(x_{1m},\dots,x_{3N_m};\mathbf{R}_0^m)\\ &\times R_k^m(x_{1m},\dots,x_{3N_m};\mathbf{R}_0^m)+\dots\Bigg),\end{aligned} \qquad (3)$$

where f_{ij}^m, f_{ijk}^m are quadratic and cubic force constants of molecule m with respect to the internal coordinates $R_i^m, i=1,\dots,3N_m-6$ and $\mathbf{R}_m^0$ is the minimum energy configuration of molecule m. The molecules in the cluster are completely decoupled.

2.2 Intermolecular potential

Solving the electronic Schrödinger equation not only gives the energy eigenvalue but also the electronic wave function of a molecule. The electronic wave functions of the molecular minimum configurations are used to determine the intermolecular interactions in a perturbational approach

$$H^{\mathrm{tot}}=\sum_m H_m+U, \qquad (4)$$

where H^{tot} is the cluster Hamiltonian, H_m is the electronic Hamiltonian of molecule m in the minimum configuration and U describes all interactions between the molecules.

The unperturbed cluster Hamiltonian is given by $H^{(0)}=\sum H_m$, the unperturbed electronic cluster wave function is the product over all electronic molecular wave functions. In second order perturbation theory the intermolecular interaction energy is typically split into the following four terms

$$U\approx V^{\mathrm{int}}=\underbrace{V^{\mathrm{elec}}+V^{\mathrm{rep}}}_{\text{1st order}}\quad+\quad\underbrace{V^{\mathrm{ind}}+V^{\mathrm{disp}}}_{\text{2nd order}}, \qquad (5)$$

where V^{elec} and V^{rep} are first order terms and describe the electrostatic interaction energy of the permanent charge distributions and the repulsion energy due to the overlap of the charge distributions. V^{ind} and V^{disp} are second order terms and describe the induction and the dispersion energy. However, at this point we are more concerned about the analytical representation of V^{int}. Typically effective two-body interactions are sufficient, sometimes three-body and higher interactions are used.

$$\begin{aligned}V^{\mathrm{int}}=&\sum_{m}^{M}\sum_{n<m}^{M}u_{mn}(\tau_m,\tau_n)\\ &+\sum_{m}^{M}\sum_{n<m}^{M}\sum_{o<n}^{M}u_{mno}(\tau_m,\tau_n,\tau_o)+\ \dots\ ,\end{aligned} \qquad (6)$$

where u_{mn} and u_{mno} denote molecular two-body and three-body interactions and τ_m represents the center of mass position and the orientation of molecule m. The functions u_{mn} and u_{mno} can be represented by

$$u_{mn}(\tau_m,\tau_n) = \sum_a^{N_m}\sum_b^{N_n} v_{ab}^{mn}\left(R_a^m(\tau_m), R_b^n(\tau_n)\right)$$

$$+\sum_a^{N_m}\sum_b^{N_n}\sum_c^{N_n} v_{abc}^{mn}\left(R_a^m(\tau_m), R_b^n(\tau_n), R_c^n(\tau_n)\right) + \ldots \quad (7)$$

$$u_{mno}(\tau_m,\tau_n,\tau_o) = \sum_a^{N_m}\sum_b^{N_n}\sum_c^{N_o} v_{abc}^{mno}$$

$$\times\left(R_a^m(\tau_m), R_b^n(\tau_n), R_c^o(\tau_o)\right) + \ldots, \quad (8)$$

where v_{ab}^{mn} denotes two-body interactions between site a in molecule m and site b in molecule n, v_{abc}^{mn} denotes three-body interactions between sites a, b, and c in molecules m and n, and v_{abc}^{mno} denotes three-body interactions between sites a, b, and c in molecules m, n, and o. $R_a^m(\tau_m)$ is the position of site a in molecule m and depends on the orientation and center of mass position τ_m of molecule m. Introducing $\sum_{m=1}^{M} N_m$ boundary conditions which guarantee the geometry of the molecules, equation (6) can be rewritten as

$$V^{\text{int}} = \sum_m^M \sum_{n<m}^M \left(\sum_a^{N_m}\sum_b^{N_n} v_{ab}^{mn}\left(R_a^m, R_b^n\right) + \ldots\right) \quad (9)$$

$$+\sum_m^M \sum_{n<m}^M \sum_{o<n}^M \left(\sum_a^{N_m}\sum_b^{N_n}\sum_c^{N_o} v_{abc}^{mno}\left(R_a^m, R_b^n, R_c^o\right) + \ldots\right) + \ldots$$

and

$$R_a^m - {}^0R_a^m = 0 \qquad a = 1,\ldots,N_m\,, \qquad m = 1,\ldots,M, \quad (10)$$

where ${}^0R_a^m$ is the position of site a in molecule m in the minimum configuration. There is no difficulty in finding all necessary boundary conditions, because we can simply use the definitions of the internal coordinates. At this point we can introduce a formal extension to V^{int}

$$V^{\text{int}} = \sum_m^M \left(\sum_a^{N_m}\sum_{b<a}^{N_m} v_{ab}^{m}\left(R_a^m, R_b^m\right)\right.$$

$$\left. + \sum_a^{N_m}\sum_{b<a}^{N_m}\sum_{c<b}^{N_m} v_{abc}^{m}\left(R_a^m, R_b^m, R_c^m\right) + \ldots\right)$$

$$+\sum_m^M \sum_{n<m}^M \left(\sum_a^{N_m}\sum_b^{N_n} v_{ab}^{mn}\left(R_a^m, R_b^n\right) + \ldots\right) \quad (11)$$

$$+\sum_m^M \sum_{n<m}^M \sum_{o<n}^M \left(\sum_a^{N_m}\sum_b^{N_n}\sum_c^{N_o} v_{abc}^{mno}\left(R_a^m, R_b^n, R_c^o\right) + \ldots\right) + \ldots$$

and

$$R_a^m - {}^0R_a^m = 0 \qquad a = 1,\ldots,N_m\,, \qquad m = 1,\ldots,M, \quad (12)$$

since the expression in the first line is equal to zero as long as the boundary conditions hold true. We can easily identify the intramolecular interactions in this term. Inserting the intramolecular force fields of equation (3) into this expression and lifting all boundary conditions of equations (12) defines the total cluster potential V^{tot}. After some rearranging V^{tot} can be written as

$$V^{\text{tot}} = \sum_a^N \sum_{b<a}^N V_{ab}(R_a, R_b)$$

$$+\sum_a^N \sum_{b<a}^N \sum_{c<b}^N V_{abc}(R_a, R_b, R_c) + \ldots, \quad (13)$$

where N is the number of interaction sites in the cluster and V_{ab}, V_{abc} denote two-body and three-body site-site interactions in the cluster.

We speak of tuned intra- and intermolecular potentials, if both types of models depend on the same set of interaction sites. As we are interested in vibrations of the atomic nuclei typically those models are of interest that explicitly depend on the atomic sites which determine the vibrations of interest. Ideally for each atomic nucleus a potential site is defined.

Unfortunately intra- and intermolecular potentials are usually not tuned to each other so that further approximations have to be introduced. **1)** The molecular minimum configurations $\mathbf{R}_0^m$ are not the same for the intra- and intermolecular potential. Approximation: transferability of potential parameters for their use with a slightly different molecular geometry. **2)** The intra- or the intermolecular potential is parametrized with respect to only some of the atomic nuclei. Approximation: the easiest approach is to simplify the more complete potential until the intra- and intermolecular potentials are tuned. **3)** For the intermolecular potential additional interaction sites are defined that are not located on atomic nuclei. Approximation: interactions with these sites have to be formulated as functions of the atomic nuclei.

3 Spectroscopic methods based on normal modes

Using the total cluster potential V^{tot} of equation (13) standard spectroscopic methods can be applied to calculate the vibrational energy levels. First of all, the minima on the total cluster PES are needed. Since the determination of the global minimum requires the calculation of many local minima, this can be quite a time consuming task. Therefore we suggest a stepwise procedure: in the first step we calculate minima on the intermolecular PES $V^{\text{int}}(\tau_1,\ldots,\tau_M)$. This reduces the dimension of the configurational space drastically and therefore saves a large amount of computer time. Nevertheless the most important features of the potential that determine the cluster structure are included. Local minimum configurations $(\tau_1, \dots, \tau_M)$ serve as input for the total cluster PES. In the second step we further minimize the input configuration on the total cluster PES. Usually only minor configurational changes occur during the second minimization step. However, some cluster configurations may be unstable and disappear while others may be distorted in an unphysical way. Unstable structures are interesting, since their disappearance may change the interpretation of an experimental spectrum. Unphysical distortion of structures merely indicates the breakdown of the potential ansatz.

3.1 Normal mode analysis

To calculate the harmonic vibrational energy eigenvalues the total cluster potential V^{tot} is expanded in a series around the global minimum configuration. In principle, it is possible at this point to introduce further internal coordinates for the intermolecular degrees of freedom and to expand the series with respect to the internal coordinates of the cluster. Wilson's FG-method would be the standard scheme to solve this problem [12]. The most important reason for using internal coordinates is the improved convergence of the total potential energy and a weaker coupling between these coordinates in comparison with (mass-weighted) Cartesian coordinates. Furthermore, translational and rotational motion of the cluster is excluded from the problem. Certainly, when using expensive *ab initio* force fields the choice of internal coordinates is appropriate. However, we are using a comparatively crude PES. Therefore and because of the tremendous simplification of the problem, we prefer the expansion of the total cluster PES in mass-weighted Cartesian coordinates up to quadratic terms

$$d_i = \sqrt{m_i}(x_i - x_i^0), \qquad i = 1, \dots, 3N. \tag{14}$$

Especially we are thus saving the introduction of internal coordinates for the intermolecular degrees of freedom for each cluster size and, in general, even for each isomer.

The cluster Hamiltonian is given by

$$\begin{aligned} H &= T + V & (15)\\ &= \frac{1}{2}\sum_i \dot{\underline{\mathrm{d}}}_i^T \dot{\underline{\mathrm{d}}}_i + \frac{1}{2}\sum_{i,j} \underline{\mathrm{d}}_i^T \underline{\underline{\mathrm{F}}}\, \underline{\mathrm{d}}_j & (16)\\ &= \frac{1}{2}\sum_i (\dot{\underline{\mathrm{Q}}}_i^T \dot{\underline{\mathrm{Q}}}_i) + \frac{1}{2}\sum_i (\underline{\mathrm{Q}}_i^T \underline{\underline{\mathit{\Lambda}}}\, \underline{\mathrm{Q}}_j), & (17) \end{aligned}$$

where $\underline{\underline{\mathrm{F}}}$ is the quadratic force constant matrix $\left(\frac{\partial^2 V^{\mathrm{tot}}}{\partial d_i \partial d_j}\right)_{i,j}$ which is calculated numerically using an $O(h^4)$ algorithm, which is presented in Appendix A, Q_i is a normal coordinate, and $\underline{\underline{\mathrm{l}}}$ is the linear transformation matrix that connects mass-weighted Cartesian coordinates with normal coordinates

$$\underline{\mathrm{d}} = \underline{\underline{\mathrm{l}}}\,\underline{\mathrm{Q}}. \tag{18}$$

The matrix $\underline{\underline{\mathit{\Lambda}}} = \underline{\underline{\mathrm{l}}}^T \underline{\underline{\mathrm{F}}}\, \underline{\underline{\mathrm{l}}}$ is diagonal and contains the eigenvalues ω_i^2. Since normal coordinates $\underline{Q}_i$ and $\underline{Q}_j$ are orthogonal, the harmonic cluster Hamiltonian can be written as

$$H = \frac{1}{2}\sum_i \left(\dot{Q}_i^2 + \omega_i^2 Q_i^2\right). \tag{19}$$

The eigenvalues ω_i^2 and the linear transformation matrix $\underline{\underline{\mathrm{l}}}$ are calculated numerically using, for example, the Jacobi or the Householder algorithm. Both algorithms produce orthogonal matrices even for degenerate modes, which will be of importance for the anharmonic treatment of degenerate terms.

At this point it seems appropriate to introduce dimensionless normal coordinates q_i and their conjugate momenta p_i for obvious reasons

$$\underline{q}_i = \sum_{a=1}^{3N} l_{ia} \sqrt{\frac{2\pi c\omega_i}{\hbar}} A_a \hat{\underline{d}}_a = \sqrt{\frac{2\pi c\omega_i}{\hbar}} \underline{Q}_i \quad \text{and} \tag{20}$$

$$\underline{p}_i = \sum_{a=1}^{3N} l_{ia} \sqrt{\frac{1}{2\pi\hbar c\omega_i}} \dot{A}_a \hat{\underline{d}}_a = \sqrt{\frac{1}{2\pi\hbar c\omega_i}} \underline{P}_i, \tag{21}$$

where $\hat{\underline{d}}_a$ is a Cartesian unit vector and A_a, $\dot{A}_a$ are amplitudes. Typically units are chosen so that ω_i is given in wavenumbers. In dimensionless normal coordinates the vibrational harmonic Hamiltonian is given by

$$\frac{hc}{2}\sum_{i=1}^{3N-6} \omega_i \left(p_i^2 + q_i^2\right). \tag{22}$$

3.2 Anharmonic corrections

Often there is only a rather poor agreement between experimental and theoretical values in the harmonic approximation. Therefore an expansion of V^{tot} with respect to normal coordinates is required that includes cubic and higher terms. Since V^{tot} is given as a function of mass-weighted Cartesian coordinates we have to calculate

$$\begin{aligned} V^{\mathrm{tot}} = &\frac{1}{2}\sum_{i,j}\sum_{a,b} \frac{\partial^2 V^{\mathrm{tot}}}{\partial d_a \partial d_b} l_{ai} l_{bj} Q_i Q_j \\ &+ \frac{1}{6}\sum_{i,j,k}\sum_{a,b,c} \frac{\partial^3 V^{\mathrm{tot}}}{\partial d_a \partial d_b \partial d_c} l_{ai} l_{bj} l_{ck} Q_i Q_j Q_k + \dots \end{aligned} \tag{23}$$

This expression can be easily evaluated numerically, however, the calculation can be quite time consuming. We can save computer time by introducing an approximation that exploits the information given by the $\underline{\underline{l}}$-matrix. For a single derivative of $V^{\rm tot}$ with respect to q_i we find

$$\frac{\partial V^{\rm tot}}{\partial Q_i} \approx \frac{V^{\rm tot}(\underline{\rm d}_0 + h\sum_a l_{ia}\hat{\underline{\rm d}}_a) - V^{\rm tot}(\underline{\rm d}_0)}{h}, \tag{24}$$

where $\underline{\rm d}_0$ denotes the minimum configuration in mass-weighted Cartesian coordinates and $\hat{\underline{\rm d}}_a$ is a unit vector. Of course, this procedure can be easily generalized to higher derivatives. Again we used a difference quotient with an error term $O(h^4)$ for the actual calculation, see Appendix A.

If cubic and quartic force constants are taken into account, an anharmonic vibrational Hamiltonian can be derived from Watson's vibration-rotation Hamiltonian which takes the form [13]

$$\frac{H}{hc} = \frac{1}{2}\sum_i \omega_i(p_i^2 + q_i^2) + \frac{1}{6}\sum_{ijk}\phi_{ijk}q_iq_jq_k + \frac{1}{24}\sum_{ijkl}\phi_{ijkl}q_iq_jq_kq_l + \sum_\alpha B_\alpha \pi_\alpha^2, \tag{25}$$

where ω_i, ϕ_{ijk}, ϕ_{ijkl} are force constants, B_α, $\alpha = x, y, z$ are the usual rotational constants (in the following course of this paper we denote them by A, B, C, where by convention $A \geq B \geq C$), and π_α denotes the vibrational angular momentum. B_α is given by

$$B_\alpha = \frac{\hbar^2}{2hcI^0_{\alpha\alpha}}, \tag{26}$$

where $I^0_{\alpha\alpha}$ denote the principle moments of inertia of the minimum configuration of the cluster. The vibrational angular momentum π_α is given by

$$\pi_\alpha = \sum_{ij}\zeta^\alpha_{ij}\sqrt{\frac{\omega_j}{\omega_i}}q_ip_j, \tag{27}$$

where $\zeta^\alpha_{ij} = \sum_k(l^\beta_{ki}l^\gamma_{kj} - l^\gamma_{ki}l^\beta_{kj})$, $\alpha, \beta, \gamma \in \{x, y, z\}$ cyclic, $i, j, k = 1, \ldots, 3N-6$ are the Coriolis coupling constants.

The Hamiltonian of equation (25) cannot be solved analytically and therefore approximative schemes have to be employed. Second order perturbation theory and a variational calculation are standard approaches and we want to mention both of them.

3.3 Perturbation approach

For asymmetric tops ($A \neq B \neq C$) non-degenerate second order perturbation theory yields vibrational energy levels [13]

$$E(\mathbf{v}) = \sum_i \omega_i\left(v_i + \frac{1}{2}\right) + \sum_{i\geq j}\chi_{ij}\left(v_i + \frac{1}{2}\right)\left(v_j + \frac{1}{2}\right) + \ldots, \tag{28}$$

where the anharmonicity constants χ_{ij} are given by

$$\chi_{ii} = \frac{1}{16}\phi_{iiii} - \frac{1}{16}\sum_k \phi^2_{iik}\frac{8\omega_i^2 - 3\omega_k^2}{\omega_k(4\omega_i^2 - \omega_k^2)} \tag{29}$$

for diagonal terms and

$$\begin{aligned}\chi_{ij} = &\frac{1}{4}\phi_{iijj} - \frac{1}{4}\sum_k \frac{\phi_{iik}\phi_{kjj}}{\omega_k} \\ &-\frac{1}{2}\sum_k \phi_{ijk}\frac{\omega_k(\omega_k^2 - \omega_i^2 - \omega_j^2)}{\Delta_{ijk}} \\ &+\left\{A(\zeta^a_{ij})^2 + B(\zeta^b_{ij})^2 + C(\zeta^c_{ij})^2\right\}\left(\frac{\omega_j}{\omega_i} + \frac{\omega_i}{\omega_j}\right)\end{aligned} \tag{30}$$

for off-diagonal terms and

$$\begin{aligned}\Delta_{ijk} = &(\omega_i + \omega_j + \omega_k)(\omega_i - \omega_j - \omega_k) \\ &\times(-\omega_i + \omega_j - \omega_k)(-\omega_i - \omega_j + \omega_k).\end{aligned} \tag{31}$$

For symmetric tops with vibrational energy levels of twofold degeneracy formulae were developed that are similar in structure to equations (28-31) [13], but nevertheless they are more complicate and more difficult to handle in a computer program. It is, however, unnecessary to use them as long as routines are employed for the diagonalization of the quadratic force constant matrix $\underline{\underline{F}}$ that produce an orthogonal transformation matrix $\underline{\underline{l}}$. Although we partly used the explicit formulae for twofold degeneracies given in [13] we do not recommend their use.

3.4 Accidental degeneracies

Inspection of the denominator Δ_{ijk} in equation (30) reveals the well-known fact that Fermi resonances may lead to at least a partial breakdown of the perturbational treatment. To avoid the most probable Fermi resonances, we therefore used a simplified Hamiltonian for intramolecular line shift calculations that neglects all couplings induced by cubic and quartic force constants between intra- and intermolecular modes. Rotationally induced couplings are included, however.

$$\begin{aligned}H = &\sum_{m=1}^{M}\left(\frac{1}{2}\sum_{a=1}^{3N_m-6}\omega_{a,m}(p^2_{a,m} + q^2_{a,m})\right) \\ &+\sum_{m,n,o=1}^{M}\left(\frac{1}{6}\sum_{a=1}^{3N_m-6}\sum_{b=1}^{3N_n-6}\sum_{c=1}^{3N_o-6}\phi_{abc,mno}q_{a,m}q_{b,n}q_{c,o}\right) \\ &+\sum_{m,n=1}^{M}\left(\frac{1}{24}\sum_{a=1}^{3N_m-6}\sum_{b=1}^{3N_n-6}\phi_{aabb,mn}q^2_{a,m}q^2_{b,n}\right) + \sum_\alpha B_\alpha\pi^2_\alpha,\end{aligned} \tag{32}$$

where $\omega_{a,m}$, $\phi_{abc,mno}$, $\phi_{aabb,mn}$ denote "intramolecular" modes and force constants, respectively. Only quartic force constants $\phi_{aabb,mn}$ are calculated, following the perturbational result in equations (28-31).

3.5 Variational approach

The ansatz of equation (32) reduces the number of possible Fermi resonances drastically, however, they do not disappear. Therefore we alternatively employed the linear variational ansatz

$$\chi = \sum_a c_a |u_a\rangle, \tag{33}$$

for the vibrational wave function χ, where c_a are parameters that have to be determined and $|u_a\rangle$ is given by

$$|v_{1,1}\, v_{2,1}\, \ldots\, , v_{3N_M-6,M}\rangle = \prod_{m=1}^{M} \prod_{a=1}^{N_m-6} |v_{a,m}\rangle, \tag{34}$$

where $|v_{a,m}\rangle$ denotes the one dimensional state of normal mode a localized in molecule m. For the actual calculation of the eigenvalue problem

$$\det(\langle v_b|H|v_a\rangle - E\delta_{ab}) = 0 \tag{35}$$

the Hamiltonian matrix of equation (32) is still too large. We therefore built up and diagonalized a matrix for each mode a in molecule m that is of interest

$$\begin{aligned} H^{\text{var}} &= \frac{1}{2}\omega_{a,m}(p_{a,m}^2 + q_{a,m}^2) \\ &+ \sum_{n,o=1}^{M} \left(\frac{1}{6} \sum_{b=1}^{3N_n-6} \sum_{c=1}^{3N_o-6} \phi_{abc,mno} q_{a,m} q_{b,n} q_{c,o} \right) \\ &+ \sum_{n=1}^{M} \left(\frac{1}{24} \sum_{b=1}^{3N_n-6} \phi_{aabb,mn} q_{a,m}^2 q_{b,n}^2 \right). \end{aligned} \tag{36}$$

The rotational influence on the vibrational energy levels $\sum_\alpha B_\alpha \pi_\alpha^2$ is still taken into account *via* perturbation theory.

As regards the number of states which we are taking into account in our calculation we distinguish between mode $\omega_{a,m}$ of interest with quantum number $v_{a,m} \leq n_{a,m}$ and all other modes $\omega_{b,n}$ $(b \neq a \wedge n \neq m)$ with quantum numbers $v_{b,n} \leq n$. All diagonal matrix elements

$$\langle v_{a,m}\, v_{b,n}|H^{\text{var}}|v_{a,m}\, v_{b,n}\rangle$$

and

$$\langle v_{a,m}\, v_{b,n} = 1\, v_{c,o} = 1|H^{\text{var}}|v_{a,m}\, v_{b,n} = 1\, v_{c,o} = 1\rangle$$

$(b \neq a \wedge n \neq m; c \neq a \wedge o \neq m; b \neq c \wedge n \neq o)$ are taken into account and their corresponding off-diagonal terms. For a cluster consisting of different types of molecules the number $\mathcal{N}$ of harmonic oscillator basis functions which we are taking into account is given by

$$\begin{aligned} \mathcal{N} = (n_{a,m} + 1) &\left\{ 1 + n \left(\sum_{m=1}^{M} (3N_m - 6) \right) \right. \\ &+ \left. \frac{1}{2} \left(\sum_{m=1}^{M} (3N_m - 6) - 1 \right) \left(\sum_{m'=1}^{M} (3N_{m'} - 6) - 2 \right) \right\}. \end{aligned} \tag{37}$$

This expression simplifies for a cluster of identical molecules to

$$\begin{aligned} \mathcal{N} = (n_{a,m} + 1) &\left\{ 2 - n \right. \\ &+ \left. M(3N - 6) \left(n + \frac{M(3N-6) - 3}{2} \right) \right\}. \end{aligned} \tag{38}$$

For all results given in Section 4, $n_{a,m} = n = 4$ was chosen.

3.6 Infrared intensities

The infrared intensity in the harmonic approximation of a fundamental excitation is proportional to $\langle v_{a,m} = 1|\underline{\mu}_{\text{clu}}|v_{a,m} = 0\rangle$, where $\underline{\mu}_{\text{clu}}$ is the dipole moment operator as a function of normal coordinates. Under the assumption that the charge distribution is described by partial charges c_i on the atomic interaction sites which do not vary for small deviations from their original positions, this expression may be written as

$$\begin{aligned} &\langle v_{a,m} = 1|\underline{\mu}_{\text{clu}}|v_{a,m} = 0\rangle \\ &= \left\langle v_{a,m} = 1 \left| \underline{\mu}_0 + \sum_{i=1}^{3N-6} \frac{\partial \underline{\mu}_{\text{clu}}}{\partial q_i} q_i \right| v_{a,m} = 0 \right\rangle \\ &= \frac{1}{\sqrt{2}} \sum_b \frac{\partial \underline{\mu}_{\text{clu}}}{\partial d_b} \frac{\partial d_b}{\partial q_{a,m}} \\ &= \frac{1}{\sqrt{2}} \sum_b c_b \sqrt{\frac{\hbar}{2\pi c \omega_{a,m}}}\, l_{b(a,m)} \underline{\hat{\mathrm{d}}}_b. \end{aligned} \tag{39}$$

In the following discussion only relative intensities are given.

4 Frequency shifts in small methanol clusters

4.1 Intermolecular potential

The *Optimized Potential for Liquid Simulation* (OPLS) by Jorgensen [14] for methanol was used for the intermolecular interaction which is represented analytically for two molecules m and n by

$$u_{mn} = \sum_{a \in m} \sum_{b \in n} \left(\frac{1}{4\pi\epsilon_0} \frac{c_a c_b \mathrm{e}^2}{R_{ab}} + \frac{A_{ab}}{R_{ab}^{12}} - \frac{C_{ab}}{R_{ab}^{6}} \right), \tag{40}$$

where c_a denotes a partial charge in molecule m, c_b denotes a partial charge in molecule n, R_{ab} is the distance between site a in molecule m and site b in molecule n, and A_{ab}, C_{ab} are given by the combination rules $A_{ab} = \sqrt{A_{aa} A_{bb}}$ and $C_{ab} = \sqrt{C_{aa} C_{bb}}$, where $A_{aa} = 4\epsilon_a \sigma_a^{12}$ and $C_{aa} = 4\epsilon_a \sigma_a^6$, and ϵ_a, σ_a are Lennard-Jones parameters. All potential parameters are given in Table 1.

For the construction of the interaction model, transferability of potential parameters from other models was assumed which were optimized later by fitting calculated macroscopic quantities of the liquid phase to experimental data. To effectively account for three-body forces in the liquid phase the static dipole moment was deliberately chosen too large. It overestimates the experimental value by about 25%. The geometry of the effective molecule is given in Table 2.

Cluster structures up to the hexamer were calculated by Buck and Schmidt [6]. For $M = 3{-}6$ ring structures are found for the lowest energy configurations with C_{3h}-, C_{4h}-, C_1-, and S_6-symmetry, respectively. The binding energies from dimer to hexamer are given by -28.5, -73.4, -124.8, -166.2, and -204.1 kJ mol^{-1}. The overestimated static dipole moment leads especially for the dimer to an overestimated binding energy. Minimizing the total cluster PES further increases the binding energies and yields from dimer to hexamer -29.2, -75.9, -129.9, -173.1, and -212.6 kJ mol^{-1}.

4.2 Intramolecular interaction

The anharmonic SCF force field by Schlegel *et al.* [15] is defined for all 6 atomic sites of the methanol molecule. Obviously our chosen intra- and intermolecular potentials are not tuned to each other. We follow our simple recipe of Sections 2.1 and 2.2 and simplify the intramolecular force field. Using the molecular geometry of Table 2, we take the corresponding diagonal force constants f_{aa}, f_{aaa}, and f_{aaaa} as input parameters. Only the quadratic force constants are fitted so that the anharmonic fundamental frequencies ν_1 (OH-stretch), ν_2 (COH-bend), and ν_3 (CO-stretch) are equal to the experimental gas phase values at 3681.5 cm^{-1} for the OH-stretch mode, 1334.0 cm^{-1} for the COH-bend mode and 1033.5 cm^{-1} for the CO-stretch mode using the perturbation approach of Section 2. All relevant force constants are given in Table 3.

4.3 Frequency shifts

As described above the potential model restricts us to the investigation of the OH-stretch, COH-bend, and CO-stretch mode. Experimental band shift measurements for size selected clusters are available for the CO-stretch mode from the dimer to the hexamer [5] and for the OH-stretch mode for the dimer and trimer [16,17]. In Table 4 we list all experimental results along with theoretical results in various approximations. M1 denotes results calculated within the *molecular approach* of Buck and Schmidt [6], M2 denotes the molecular approach of Beu [8], C1, C2, and C3 denote the cluster approach described in Section 2 and 3 in the harmonic (C1) and the anharmonic approximation using second order perturbation theory (C2) or a variational calculation (C3). C1SCF denotes the cluster approach in the harmonic approximation, however, using a complete SCF force field by Bleiber and Sauer [11]. Not given in the table are similar SCF results by Mó *et al.* [18] for the dimer and trimer.

Table 1. Geometrical parameters of the methanol monomer.

bond lengths	Å	bond angle	degree
O-H	0.945	COH	108.5
C-O	1.430		

Table 2. OPLS parameter values for methanol.

site	q_a, |e|	σ_a, Å	ϵ_a, kJ mole^{-1}
C	+0.265	3.84	0.799
O	−0.700	3.07	0.711
H	+0.435	–	–

Table 3. Effective force field for methanol. The effective quadratic force constants are denoted by f_{aa}^{eff}. All other values are taken from reference [15]. Quadratic and cubic bending force constants are given in mdyne Å, quadratic, cubic, and quartic stretching force constants are given in mdyne Å^{-1}, mdyne Å^{-2}, and mdyne Å^{-3}, respectively.

type	OH-str.	CO-str.	COH-bend.
f_{aa}	8.3910	5.7230	0.8440
f_{aa}^{eff}	8.2827	5.3431	0.8442
f_{aaa}	-59.8800	-31.8260	-1.4310
f_{aaaa}	420.6690	203.3250	–

In Figure 1 the experimental results are shown for the CO-stretch mode for $m = 2{-}6$ together with calculated stick spectra representing variational results (C3) for the line shifts and harmonic values for the relative intensities.

For the dimer CO-stretch mode the C1-, C2-, and C3-results are in much better agreement with the experimental values than those obtained with the *molecular approaches* M1 and M2. The line splitting is underestimated by about 35% which is in agreement with the M2 result, but the overall position of the two lines is only correct for the *cluster approaches*. Hence, especially the experimental acceptor redshift can be confirmed. The anharmonic contributions are negligible for the dimer CO-stretch modes and small for the other cluster sizes. As expected, the anharmonic contributions are more pronounced for the OH-stretch modes but still they are rather small. Although an improvement can be observed from C1 to C3 the agreement with the experimental data remains poor. The C3 donor line shift exceeds the experimental value at -107 cm^{-1} by more than 100 cm^{-1}.

Only one infrared active OH-stretch mode is found for the trimer using the OPLS-potential, however, three distinct lines are found in the experiment and using the SCF force field. The agreement between experimental and theoretical values remains poor in all cases. For the bands an almost constant line splitting of about 40 cm^{-1} is found. The C1SCF values consist of two narrow lying lines with

Table 4. Experimental band shifts of methanol clusters and theoretical values for the energetically most stable structures of the OPLS-potential. M is the cluster size, PG the molecular point group, S the symmetry of the normal mode, and $\Delta\nu$ denotes the line shift with respect to the monomer gas phase value at 1033.5 cm^{-1} for the CO-stretch mode and 3681.5 cm^{-1} for the OH-stretch mode; exp denotes experimental values taken from references [5,16,17], M1 and M2 are calculated values using the *molecular approach* taken from references [6] and [8], C1SCF are harmonic values from SCF calculations [11], and C1, C2, and C3 are values computed for this work in the harmonic approximation (C1), the anharmonic approximation using a perturbational calculation (C2) and a variational calculation (C3).

M	PG	Mode	Exp	S	$\Delta\nu$, cm^{-1}					
					M1	M2	C1SCF	C1	C2	C3
2		CO	− 7	a	1	2	− 13	− 5	− 5	− 5
			19	a	29	18	12	13	14	14
3	C_{3h}			e'	4	23		13	14	17
3	C_1		8	a			− 2, 1, 9			
4	C_{4h}		11	e_u	25	26		18	23	23
4	S_4			b			− 3			
				e			1			
5			14	a	17	24	− 3	12	14	18
				a	21	24	− 2	13	16	19
				a	28	28	3	15	18	19
				a			5	15	19	21
				a			11	16	19	22
6	S_6		7	a_u	33	23^*	− 3	10	11	15
			19	e_u	17	29^*	4	13	15	19
2		OH	− 107	a	− 239	− 222	− 78	− 261	− 234	− 211
			3	a	21	− 43	− 3	− 35	− 25	− 26
3	C_{3h}			e'				− 262	− 233	
3	C_1		− 172,− 211,− 248	a			− 116,− 120,− 150			
4	C_{4h}			e_u				− 352	− 302	
4	S_4			b			− 177			
				e			− 199			
5				a			− 194	− 347	− 295	
				a			− 201	− 348	− 296	
				a			− 227	− 379	− 323	
				a			− 234	− 379	− 323	
				a			− 274	− 410	− 349	
6	S_6			a_u			− 203	− 347	− 295	
				e_u			− 250	− 389	− 333	

*No symmetry of modes given.

a line splitting of only 5 cm^{-1} and another band at a distance of about 30 cm^{-1}. The overall band shift is underestimated by about 80 cm^{-1} with respect to the experimental evidence.

In the second lowest panel of Figure 1 only one Lorentzian curve is fitted to the experimental data measured in the region of the CO-stretch mode. However, the linewidth is remarkably broad and at about 1040 cm^{-1} and 1045 cm^{-1} structures can be observed in the data points that might be attributed to different bands.

The experimental data for the tetramer and pentamer in Figure 1 in the region of the CO-stretch mode differ in their line shift as well as in their line shape. The line width of the pentamer curve is broader than that of the tetramer curve. This corresponds to the C3-result depicted in Figure 1 in which 5 lines contribute to the experimental spectrum while only one line contributes to the tetramer spectrum. Up to the pentamer the experimental data show an increasing overall blueshift that is confirmed by the C3-values only up to the tetramer. The C1-, C2-, and C3-values overestimate the overall blueshift, however, the results obtained in the M1- and M2-approximation are improved. For the C1SCF-values two infrared active lines are found for the tetramer and five for the pentamer which both do not agree well to the experimental data.

For the hexamer there is a qualitative agreement between the experimental results in the region of the CO-stretch mode and the theoretical results, *i.e.* only two infrared active modes can be observed. In no approximation a quantitative agreement to the experimental data is achieved.

5 Discussion

A formal construction scheme has been given for a total cluster PES using decoupled intra- and intermolecular potentials. This ansatz was used previously by Reimers and Watts for the calculation of vibrational spectra of small water clusters without giving explicit formulae for the

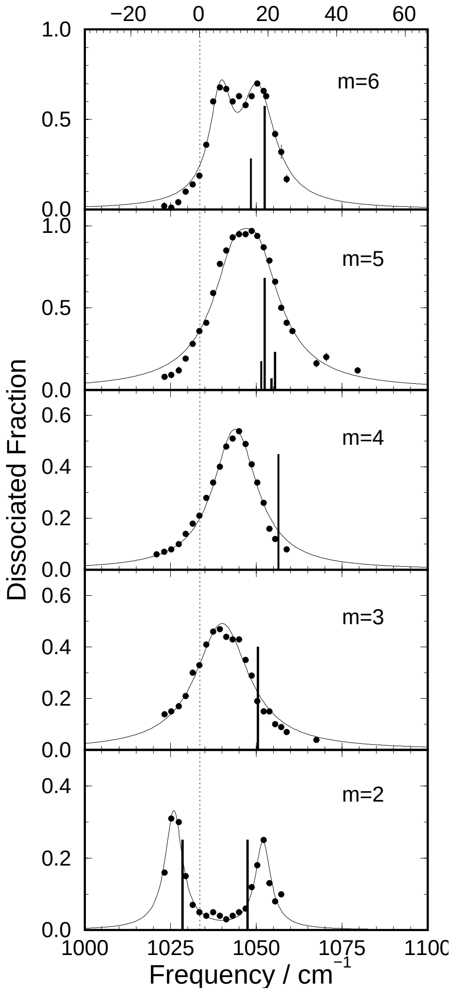

Fig. 1. Comparison of experimental data taken from reference [5] with theoretical line shift calculations in the variational approximation from dimer to hexamer for the CO stretch mode. The dotted line indicates the monomer value at 1033.5 cm^{-1}. The upper abscissa denotes line shifts with respect to the monomer value while the lower abscissa gives the absolute values.

total cluster potential [10]. Standard spectroscopic methods could be applied to calculate harmonic (C1) or anharmonic (C2 or C3) vibrational spectra and converts the procedure into a flexible theoretical instrument. Reimers and Watts introduce internal coordinates for the intermolecular degrees of freedom which requires much more effort for larger clusters than our simple approach using mass-weighted Cartesian coordinates for the representation of the total cluster PES. Since the minimization process implies a rather crude approximation of the total cluster PES, the use of mass-weighted Cartesian coordinates seems to be a justified simplification.

Reimers and Watts come to the conclusion that in the anharmonic treatment the use of local modes is preferable over normal modes. Della Valle has shown, however, that there is a mapping between a local mode Hamiltonian and a normal mode Hamiltonian including the off-diagonal terms of operators $q_a q_b q_c q_d$ [19]. The discrepancy in the results using local modes and normal modes in reference [10] can be explained by the fact that only diagonal force constants are used for the normal modes which is not sufficient, if results are compared with local modes. Therefore we recommend the use of the simpler normal modes, however, with off-diagonal terms included in the calculation.

The *molecular approach* of Beu [8] is more difficult to handle in comparison to the *cluster approach.* As long as the description of the total cluster PES by intra- and intermolecular potentials holds, results of the *cluster approach* should be more accurate, since already in the harmonic approximation the coupling of intra- and intermolecular modes is accounted for. Symmetry properties of the cluster are simply included in this approach. They make, however, complicated calculations necessary for the *molecular approach.* Intermolecular modes can easily be calculated using the total cluster PES, they are not available within the *molecular approach.*

The results obtained with the *cluster approach* (C1, C2, C3) are in much better agreement with the experimental results than those obtained with the *molecular approaches* (M1, M2). The reason for this lies not only in the methodology of the line shift calculation but also in the modification of the intramolecular potential. This stresses the necessity of the tuning process of the intra- and intermolecular input potentials.

Although considerable improvements could be achieved concerning the CO-stretch mode, objections have to be made concerning the use of the OPLS-potential. Since it is fitted mainly to properties of the liquid bulk, it might not be surprising that there are deficiencies in the microscopic range. In particular, the planarity of the lowest energy trimer with C_{3h}-symmetry and of the tetramer with C_{4h}-symmetry is somewhat questionable, since it contradicts the idea of a linear hydrogen bond in small methanol clusters. The simple reason is that in a planar ring it is impossible to define a unique hydrogen bond, since the tetrahedral structure of the sp^3-orbitals of the oxygen atoms offers the choice between two equivalent bonds. Hence we expect a distinct deviation from a planar ring structure as is found, for example, for the pentamer and the hexamer. Furthermore SCF calculations confirm for the energetically most stable structures a distorted ring for the trimer and a ring with S_4-symmetry for the tetramer [11, 18]. Experimental results for the OH-stretch mode [17] clearly show that a planar ring configuration is not observed. For water clusters, for which a similar electronic structure of the O-atoms is found, non-planar structures for the lowest energy trimer and tetramer configurations were found [10,20]. One important conclusion is that the OPLS-potential represents the anisotropy especially of the electrostatic part of the intermolecular methanol interaction only unsatisfactory.

In Section 4 we found surprisingly small anharmonic corrections especially for the OH-stretch mode. This may partly be attributed to the unrealistic repulsive part of the OPLS-potential which exaggerates the steepness of the repulsive branch of the interaction potential. For the static dipole moment of the OPLS-model, which was chosen to exceed the experimental value by about 25%, it is noted that this could be useful for the simulation of liquid bulk properties. There are, however, serious consequences for the OH-stretch mode of the donor molecule, since the hydrogen atoms are directly bound in the hydrogen bond which may partly explain the large deviation from the experimental donor frequency shift by more than 100 cm^{-1} for the dimer.

Table 4 shows that especially for the dimer OH-stretch mode the harmonic SCF-values are in better agreement with the experimental values than those calculated with the OPLS-potential. The general agreement, however, between the experimental data and the theoretical values is still rather poor. An anharmonic treatment seems necessary even for the CO-stretch modes and it is mandatory for the OH-stretch mode. On the other hand, it is too expensive to calculate an anharmonic force field for large clusters. The basis set superposition error is a severe problem which might be avoided, if one uses intermolecular potentials that are based on monomer wave functions only. Therefore it seems quite competitive to use precise intermolecular potential models in combination with intramolecular force fields. The intermolecular potential model may even include correlation effects by fitting calculated properties to experimental data and thereby improving the appropriate potential parameters. An approach along these lines is in preparation and will appear soon [21].

We conclude that the cluster approach is a flexible instrument for calculating cluster frequencies for intramolecular as well as intermolecular modes. For methanol a more sophisticated intermolecular potential model is needed that incorporates a better representation of the electrostatic interaction and a more realistic functional description of the repulsive interaction.

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Appendix A

Numerical differentiation formulae

It proved necessary during our investigation to put some effort into the calculation of the numerical force constants of equations (16, 32). A convenient method is based on a variant of the Lagrange interpolation formula for equal intervals given by [22]

$$f(x)=\frac{(-1)^n t(t-1)\dots(t-n)}{n!}\sum_{i=0}^{n}\frac{(-1)^i C_n^i y_i}{t-i}$$
$$+h^{n+1}t(t-1)\dots(t-n)f(x;x_0;x_1;\dots;x_n), \quad (41)$$

where $t=\frac{x-x_0}{h}$ and therefore $\mathrm{d}x = h\,\mathrm{d}t$. $n+1$ is the number of nodes, C_n^i denotes the binomial coefficient and y_i is the functional value at node x_i. The cluster potential function is approximated by the Lagrange polynomial in the minimum configuration for which analytical derivatives easily can be calculated. The number of nodes taken into account determines the error term and the computer time that is needed for the calculation.

$O(h^4)$ *formulae*

$$y_2^{(1)} = \frac{1}{12h}[y_0-8y_1+8y_2-y_3]+O(h^4), \quad (42)$$
$$y_2^{(2)} = \frac{1}{24h^2}[-2y_0+32y_1-60y_2+32y_3-2y_4]+O(h^4), \quad (43)$$
$$y_3^{(3)} = \frac{1}{8h^3}[y_0-8y_1+13y_2-13y_4+8y_5+y_6]+O(h^4), \quad (44)$$
$$y_3^{(4)} = \frac{1}{6h^4}[-y_0+12y_1-39y_4+12y_5-y_6]+O(h^4). \quad (45)$$

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