Hexapole transmission spectrum of formaldehyde oxide

5 AUTHORS, INCLUDING:

W.G. Roeterdink
Jilin University
39 PUBLICATIONS **403** CITATIONS

SEE PROFILE

Dajun Ding
Jilin University
109 PUBLICATIONS **564** CITATIONS

SEE PROFILE

Craig A Taatjes
Sandia National Laboratories
200 PUBLICATIONS **4,446** CITATIONS

SEE PROFILE

Hexapole transmission spectrum of formaldehyde oxide

W.G. Roeterdink [a,*], J. Bulthuis [b], E.P.F. Lee [c,d], D. Ding [a], C.A. Taatjes [e,f]

[a] Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, PR China
[b] Institute for Lasers, Life, and Biophotonics, Vrije Universiteit, de Boelelaan 1083, Amsterdam 1081 HV, The Netherlands
[c] School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom
[d] Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong
[e] Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, CA 94551-0969, USA
[f] School of Chemistry, Cantock's Close, University of Bristol, Bristol BS8 1TS, United Kingdom

ABSTRACT

In this theoretical study we explore the feasibility to obtain molecular properties of the Criegee intermediate formaldehyde oxide (CH_2OO) with hexapole state selection. Ab-initio calculations yielding the rotational constants and dipole moments of formaldehyde oxide are used as input for the simulations. Subsequently the hexapole focusing spectra are simulated for the low field seeking states. The focusing curves are sensitive to the details of the dipole moment, suggesting that the hexapole can be a useful tool to study the molecular properties of formaldehyde oxide, or potentially to select CH_2OO for molecular beam scattering or photodissociation measurements.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Hexapole focusing and state selection are powerful tools to isolate and orient specific components of a molecular beam. The hexapole state selection technique was initially explored for molecules with a first order Stark effect, because the force that draws such molecules towards the hexapole axis is linear in the electric field. Symmetric top molecules and linear molecules with an unpaired electron can be focused with the hexapole via the first order Stark effect [1–6]. Additionally linear molecules, such as OCS and N_2O, with l-doubled excited vibrational states can also be focused via the first order Stark effect [7–10]. Asymmetric top molecules can, in principle, be focused by the second order Stark effect and it is sometimes possible to use the hexapole for these types of molecules [11,12]. Studies in which the hexapole is used to focus symmetric top and linear molecules far outnumber those employing asymmetric top molecules. In this Letter we explore the feasibility to use the hexapole to study the molecular properties of the asymmetric top molecule formaldehyde oxide which plays an important role in atmospheric chemistry.

Unsaturated hydrocarbons can react with ozone in the troposphere, a process referred to as ozonolysis. The intermediate products in these reactions are the so called Criegee intermediates, which were postulated some sixty years ago [13]. These Criegee intermediates are elusive and until recently no direct experimental

data was available. Now, direct photoionization mass spectrometric detection of formaldehyde oxide (CH_2OO) has been reported as a product of the reaction of CH_2I with O_2, making detailed kinetics studies possible [14]. Lester et al. have employed the same method to produce CH_2OO in a molecular beam, and measured singlet O atom from CH_2OO photodissociation [15,16]. McCarthy et al. observed CH_2OO in a supersonic expansion from a methane discharge [17]. Measurement of bimolecular reaction dynamics of CH_2OO with molecular beam scattering could require some means to distinguish or separate CH_2OO from the other potentially reactive components in the beam.

Formaldehyde oxide is a near-prolate asymmetric top with a large dipole moment. Su et al. studied formaldehyde oxide produced from the $CH_2I + O_2$ reaction in a flow reactor using transient infrared absorption [18]. The vibrational frequencies they found are more consistent with a zwitterion than with a biradical structure. CCSD(T) calculations show that CH_2OO is best described as a zwitterion with a shorter C–O bond [19]. Although the mixed biradical and zwitterionic character of the CH_2OO molecule requires appropriate multi-reference treatment, the computed vibrational frequencies obtained with the single-reference CCSD(T) method are in fair agreement with the experimental values [18]. Endo et al. employed Fourier transform microwave spectroscopy to study formaldehyde oxide and its isotopologues in a discharged supersonic jet of a mixture of CH_2Br_2 and oxygen[20]. Additionally CCSD(T)-F12 calculations were performed to obtain the rotational constants at the experimental equilibrium geometry. A comparison between experiment and theory showed that the OCH angles

deviate largely from theory which might be caused by the conditions of the discharge. Because the Criegee intermediate itself has only recently been directly detected, most structural information was obtained via quantum mechanical calculations [19]. A very successful method to calculate bonding lengths and bonding angles of small molecules is the Coupled-Cluster Single–Double plus perturbative triples method with Complete Basis Set extrapolation, CCSD(T)/CBS [21]. However, the method neglects higher order correlations, core electrons are considered to be frozen and are not correlated with the valence electrons. In molecules with a "quasi" degenerate ground state or low lying excited states Multi-Reference Configuration Interaction (MRCI) methods give in general more accurate results. Coupled cluster theory and multi-configuration self-consistent field calculations show that the C–O bonding distance is about 1.275 Å and the O–O bonding distance is about 1.349 Å. These calculations are corroborated by density functional theory calculations which yield 1.254 Å and 1.351 Å, respectively, using the hybrid B3LYP functional [19].

In Section 2 the computational methods used here to calculate the rotational constants and the dipole moments are discussed. In the second part of Section 2 the theory of the Stark effect for asymmetric top molecules is briefly described. Subsequently the method to obtain the focusing spectrum of the hexapole is discussed. In Section 3 the results of the computational methods are presented, followed by the calculated Stark effect curves and the hexapole focusing spectra.

2. Computational methods and theory

Three levels of ab-initio calculation were employed to compute the dipole moments of formaldehyde oxide:

(1) The Complete Active Space Self Consistent Field (CASSCF) method with two active spaces, namely CAS(12,11) i.e., twelve electrons in eleven molecular orbitals (eight a' and three a'' orbitals), and CAS(8,7) i.e., eight electrons in seven molecular orbitals (four a' and three a'' orbitals) [22].

(2) The post-CASSCF internally contracted Multi-Reference Configuration Interaction (MRCI) method with the corresponding CASSCF active spaces: With the CAS(12,11) active space, the subsequent MRCI calculations were only possible with the aug-cc-pVDZ basis set, because with the aug-cc-pVTZ basis set, the CAS(12,11)/MRCI calculations are too large (the total numbers of contracted and uncontracted configurations are 122216980 and 14330538615, respectively) for the computational resource available to us. Nevertheless, with the CAS(8,7) active space, MRCI calculations have been performed using basis sets of up to aug-cc-pV5Z quality (the total number of contracted and uncontracted configurations are 15525174 and 1996540362, respectively) [23].

(3) The Coupled Cluster Single Double (CCSD) method [24]. The standard aug-cc-pVXZ basis sets, where $X = D, T, Q$ or 5, were used [25,26]. Extrapolation to the Complete Basis Set (CBS) limit was carried out using the X^{-3} formula and the computed dipole moments obtained with the aug-cc-pVQZ and aug-cc-pV5Z basis sets [27]. All ab-initio calculations were performed using the MOLPRO suite of programs [28,29]. The dipole moments used in this Letter to compute the Stark interaction are the CBS values obtained at the MRCI and CCSD levels.

The calculation of the Stark interaction in asymmetric top molecules has been described before and only a brief description will be given here [11,30]. The calculation in this Letter uses symmetric top functions $|JKM\rangle$ as the basis set to describe the asymmetric top eigenfunctions. The Hamiltonian is set up the following way:

The diagonal elements of the Hamiltonian for a prolate symmetric top are given by [31]:

$$\langle JKM|\mathcal{H}_{rot}|JKM\rangle = \frac{1}{2}(B+C)[J(J+1)-K^2]+AK^2 \quad (1)$$

in which A, B and C are the rotational constants. In symmetric top molecules, with only a dipole moment along the symmetry axis, the electric field (E) mixes free rotor basis functions with different J but equal K and M values [5]:

$$\mu E\langle J'KM|\cos(\theta)|JKM\rangle = \mu E(-1)^{M-K}\sqrt{(2J+1)(2J'+1)}\begin{pmatrix} J & 1 & J' \\ -M & 0 & M \end{pmatrix}\begin{pmatrix} J & 1 & J' \\ -K & 0 & K \end{pmatrix} \quad (2)$$

where Wigner 3-j Symbols are used and $H_{\mu E} = -\mu E \cos(\theta)$. The selection rules follow directly from the properties of the Wigner 3-j Symbols. In asymmetric top molecules the K states are mixed because of the asymmetry [31]:

$$\langle JKM|H_{rot}|JK\pm 2M\rangle = \frac{1}{4}(B-C)$$
$$\times\sqrt{[J(J+1)-K(K\pm 1)][J(J+1)-(K\pm 1)(K\pm 2)]} \quad (3)$$

in which B and C are the rotational constants. Even or odd K levels which differ by two interact with each other and hence is the K quantum number not a good quantum number in asymmetric top molecules. Moreover, in asymmetric top molecules, the dipole moment will, in general, not be along one of the inertial axes, let alone along the principal axis. If the molecule is planar, the z and x axes can be chosen to define this plane. Then, using spherical tensor algebra, the imaginary y part of the Hamiltonian can be avoided for computational convenience, and the $\mu_x E$ part of the dipole-field interaction can be written as:

$$\langle J'K'M|\sin(\theta)\cos(\phi)|JKM\rangle = (-1)^{M-K}\sqrt{(2J+1)(2J'+1)}\begin{pmatrix} J & 1 & J' \\ -M & 0 & M \end{pmatrix}\begin{pmatrix} J & 1 & J' \\ -K & \pm 1 & K' \end{pmatrix} \quad (4)$$

where Wigner 3-j Symbols are used. The diagonalization of the Hamiltonian is carried out with the help of the Jacobi method [32]. The Hamiltonian matrix is truncated at $J = 12$, which is sufficient to lead to convergence of the energies of the $J = 0$ to 3 states. Then for each M the size of the matrix is 169×169, since the mixing of K-states according to Eq. (4) must be allowed for.

The trajectories in the hexapole are calculated with the help of Newton's equation [5]:

$$\frac{d^2r}{dt^2} = \frac{-1}{m}\frac{\partial W}{\partial r} = \frac{-1}{m}\frac{dW}{dE}\frac{\partial E}{\partial r} \quad (5)$$

in which r is the radial distance from the center of the hexapole, W is the Stark energy at a given electric field E as calculated in the previous paragraph and m is the mass of the molecule. The dependence of the Stark energy W on the electric field E can be very accurately approximated by a series of Chebyshev polynomials [32]. The derivative dW/dE can subsequently be found by differentiating this series term by term yielding another Chebyshev series. In this calculation 100 Chebyshev coefficients have been used to accurately approximate the derivative dW/dE. The radial dependence of the electric field is given by the ideal hexapole approximation [5]:

$$\frac{\partial E}{\partial r} = \frac{6U_0}{r_0^3}r \quad (6)$$

in which U_0 is the voltage on the hexapole rods and r_0 the internal diameter of the hexapole. Eq. (5) is integrated with a fourth order

Runge–Kutta routine [32]. Convergence was found with about 175 integration steps over the length of the hexapole.

3. Results and discussion

Section 2 shows that the Stark effect in formaldehyde oxide is a function of the rotational constants and all the dipole moments of the molecule. The rotational constants directly reflect the geometry of the molecule and can be calculated when the relevant geometrical parameters of the molecule are known. Nevertheless, it should be noted that, while a set of geometrical parameters will yield a unique set of rotational constants, more than one set of geometrical parameters may be derived from a set of rotational constants. In addition, the equilibrium (r_e) geometry of a molecule is generally different from the vibrationally averaged (r_0) geometry. Endo et al. studied formaldehyde oxide experimentally using a discharged supersonic beam with a co-expansion of CH_2Br_2 and oxygen [20]. Additionally they performed a calculation at the CCSD(T)-F12/AV5Z level. A comparison between experiment and theory showed that the OCH angles deviate largely from theory which might be caused by the conditions of the discharge. Consequently a second fit to the experimental data with a fixed OCH angle to the theoretical values was made (labeled as fit 2 in their work). Generally, their fit 2 geometry is very similar to that obtained from the CCSD(T)-F12/AV5Z calculations performed by Endo et al., which were state of the art at the time. The rotational constants calculated from the optimized geometry are 2.61342, 0.41842 and 0.36068 cm^{-1} for A_e, B_e, and C_e of the normal species, respectively. These values can be compared with the experimental values (the r_0 values rather than the r_e values): 2.59355, 0.41580 and 0.35762 cm^{-1}. The differences could well be due to the vibrational averaging in the experimental values, an unavoidable issue when comparing theory (r_e) with experiment (r_0). Also, the large difference between the computed r_e OCH(trans) angle (114.86°) and the experimental fit1 value (120.80°) could well be due to the large amplitude motion of the HCO wagging mode. During the preparation of the present manuscript, McCarthy et al. reported a combined Fourier transform microwave spectroscopy and ab-initio study on CH_2OO, which is similar to that of Endo et al., except in the following [17]. Experimentally, in the work of McCarthy et al. CH_2OO was produced in an electrical discharge through a dilute mixture of CH_4/O_2, and more isotopic substituted species (than by Endo et al.) were investigated. Computationally, CCSD(T)/aug-cc-pCV5Z calculations were carried out for geometrical parameters, with ΔT and ΔQ corrections, where ΔT is the difference between CCSDT and CCSD(T) frozen core results using cc-pVTZ basis, and ΔQ is the difference between CCSDT(Q) and CCSDT frozen core results using a cc-pVDZ basis. In addition, centrifugal distortion parameters were calculated at the CCSD(T)/ANO1 level of theory, while deuterium quadrupole-coupling parameters were calculated at the CCSD(T)/cc-pCVQZ level of theory. An empirical (semi-experimental) equilibrium (r_e^{emp}) structure of CH_2OO was derived from rotational constants of nine isotopic species and zero-point vibrational corrections calculated at the CCSD(T) level of theory. Nevertheless, generally, this r_e^{emp} geometry of CH_2OO and the experimental r_0 rotational constants published by McCarthy et al. are very similar to those of Endo et al. (CCSD(T)-F12 and fit 2 geometries, and experimental r_0 rotational constants). Summarizing, the higher-level results of McCarthy et al. largely match those of Endo et al.

There are two main issues to be considered in the calculation of the dipole moments, the geometry to be used and the level of theory. For the geometry to be used there are two options:

(1) The computed CCSD(T)-F12/AV5Z geometry by Endo et al., which is very similar to the best computed and derived r_e^{emp} geometries of McCarthy et al. However, they are r_e geometries, and the corresponding r_e rotational constants differ significantly from the experimental r_0 values of McCarthy et al. and Endo et al.

(2) The fit1 geometry by Endo et al., which may be considered as an experimentally derived r_0 geometry, because the rotational constants with the fit 1 geometry agree quite well with available experimental r_0 values of Endo et al. and McCarthy et al. (better than those from computed r_e geometries). The computed dipole moments obtained using these geometries for the CCSD and the MRCI methods, both at the CBS level are shown in Table 1. The dipole moments for the geometries of McCarthy et al. lie between these two geometries, nearer to geometry 1 [17].

Higher order moments were also estimated. The calculations show that formaldehyde oxide has a molecular quadrupole of roughly -17 DÅ. The interaction Hamiltonian for the molecular quadrupole is given by the quadrupole moment times the gradient of the electric field of the hexapole. The gradient of the electric field in the hexapole can be estimated from Eq. (6) to be 169 kV/cm^2 near the rods. The maximum quadrupole interaction is about $6 \cdot 10^{-8}$ cm^{-1}, which can be neglected in our calculation.

Four Stark effect calculations are performed, using the dipole moments found from the CCSD CBS and the MRCI method using geometry 1 and 2, see Table 1. The results of the Stark effect calculation using the dipole moments obtained with the MRCI CBS method for geometry 1 are shown in Figure 1. In an asymmetric top molecule the K quantum number is not a good quantum number and a different labeling of states is needed compared to the labeling of symmetric top molecules. The asymmetric top functions are labeled by the J quantum number with two subscripts K_- and K_+. K_- denotes the value of $|K|$ in the prolate symmetric top limit ($B = C$) and K_+ the value of $|K|$ in the oblate top limit ($A = B$) [31]. Clearly the formaldehyde oxide molecule is a near prolate symmetric top molecule. The calculation of the Stark effect is a necessary ingredient to determine the trajectories in the hexapole field, see Eq. (5). The calculations show that the Stark interaction is most sensitive to the dominant dipole moment μ_z. The difference in Stark energy between the CCSD calculation with geometry 1 and MRCI calculation with geometry 2 calculation is about 0.3 cm^{-1} for the $|3_{03}>$ state in the $M = 0$ manifold at an electric field of 100 kV/cm. Figure 1 shows that the quantum states of formaldehyde oxide have a negative Stark effect at low energy, i.e., the energy of the states decreases with increasing electric field. These states are called high field seeking. In order to focus the molecule with the hexapole the radial force needs to be towards the center of the hexapole where the electric field is low. Hence we are particularly interested in the so called low field seeking states. Low field seeking states have a positive derivative of the Stark energy as a function of the electric field dW/dE. The first low field seeking state in the $M = 0$ manifold is the $|3_{03}\rangle$ state. The lowest rotational states of asymmetric top molecules with a relatively low rotational constant A are high field seeking, similar results were obtained for

Table 1
Dipole moments obtained from the calculations.

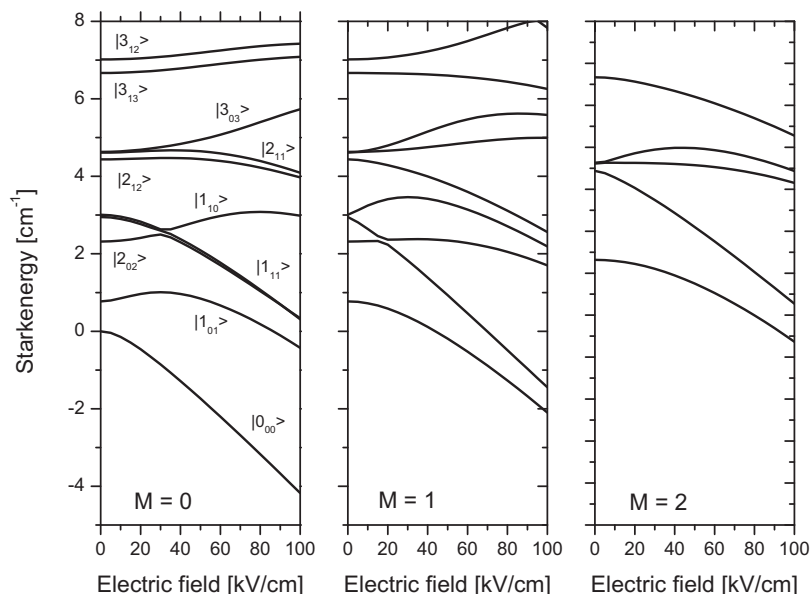| Method geometry	MRCI/CBS		CCSD(T)/CBS	
	μ_x [D]	μ_z [D]	μ_x [D]	μ_z [D]
Endo CCSD(T)-F12	0.39417	3.72396	0.41724	4.37115
Endo fit 1	0.35449	3.75496	0.39179	4.39383
McCarthy best theor	0.37901	3.74936	0.40704	4.39020
McCarthy r_e^{emp}	0.37603	3.73834	0.40346	4.37882

Figure 1. Stark curves calculated for formaldehyde oxide on the basis of the rotational constants of geometry 1 and the dipole moments from the MRCI calculation.

the CH_2F_2 molecule [11]. In contrast formaldehyde has a relatively high rotational constant A (9.40530 cm^{-1}) and the $|1_{01}\rangle$ state of the M=0 manifold is low field seeking [11].

Figure 2 shows the force constant for the indicated rotational states. The notation $|J_{K_-K_+}M\rangle$ is used to indicate the rotational levels in formaldehyde oxide, in which M is the projection of **J** on the laboratory Z-axis. The force constant is the derivative of the Stark energy as a function of the electric field divided by the magnitude of the dipole moment μ_z. In comparison the first order Stark effect in a symmetric top molecule gives the expectation value of cosine theta: $\langle\cos(\theta)\rangle = MK/J(J+1)$ which is 0.5 for the $|111\rangle$ state of a symmetric top molecule. Clearly the Stark effect in asymmetric top molecules is not linear in the electric field, reflecting the fact that asymmetric top molecules have no first order Stark effect. To a very good approximation the force constants reflect the orientation of the different rotational states of the molecule in the electric field up to 100 kV/cm. In the electric field range from 0 to 25 kV/cm, the force constants for the curves of the states

$|3_{03}0\rangle$, $|3_{12}0\rangle$ and $|3_{13}0\rangle$ are nearly linear in the electric field and reasonable peak shapes can be expected in the focus curve. The $|2_{11}0\rangle$ and $|2_{02}0\rangle$ state is low field seeking for electric fields up to 20 kV/cm but at higher electric fields it becomes high field seeking – this state cannot be focused with the hexapole characteristics used for this simulation. In our trajectory calculations we have used a hexapole with a length of 1.0 m and an internal radius of 4 mm. The maximum rod voltage needed to focus the various rotational states of formaldehyde oxide is 3 kV, yielding a maximum electric field in this hexapole of about 25 kV/cm. The difference in Stark energy for the $|3_{03}0\rangle$ state is 0.03 cm^{-1} at an electric field of 25 kV/cm and for the hexapole trajectory calculations the differences between the four dipole moment calculations are small.

To integrate formula (5) also the first derivative dr/dt must be known, which is the component of the molecular beam velocity in the radial direction. The molecular beam velocity is taken to be 565 m/s, which is the maximum expansion velocity of pure
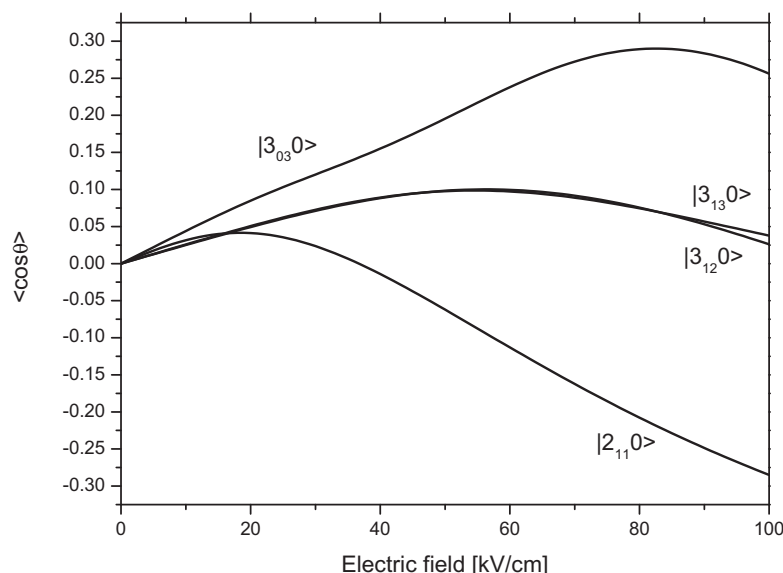

Figure 2. Force constants calculated for formaldehyde oxide on the basis of the rotational constants of geometry 1 and the dipole moments from the MRCI calculation for the indicated states.
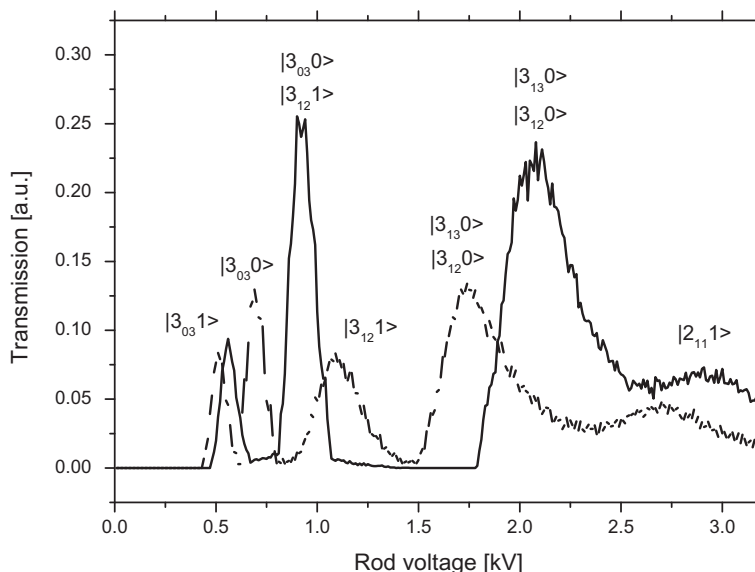
Figure 3. Transmission spectra simulated for formaldehyde oxide. The solid line represents the simulation for the geometry of Endo CCSD(T)-F12 and the dipole moments from the MRCI/CBS calculation. The dotted line represents the geometry of Endo fit1 and the dipole moments from the CCSD(T)/CBS calculation, see Table 1.

argon. The radial velocity is determined by the nozzle skimmer distance and the skimmer opening. The distance between the nozzle and the entrance of the hexapole is taken to be 30 cm. The skimmer orifice is chosen such that the whole opening angle of the hexapole is used. The speed ratio $v/\delta v$, of the molecular beam is taken to be 20. The distance from the exit of the hexapole to the focusing point is 30 cm. The computer program to calculate the trajectories is validated against the hexapole focusing spectra for CH_3I published by Ohoyama et al. [33]. In our trajectory calculations an ideal hexapole field is assumed. However, most experiments use hexapoles with cylindrical rods of diameter equal to half of the hexapole radius [5]. The non ideal effects near the hexapole rods only have a very small effect on the focus voltage for each state but do lower the transmission of the states.

Figure 3 shows the focusing spectra for CH_2OO assuming the rotational constants of geometry 1 and dipole moments of the MRCI calculation (solid line) and the rotational constants of geometry 2 and the dipole moments of the CCSD(T) calculation (dotted line). The $|3_{03}1\rangle$ peak is clearly separated from the rest at about 550 V. For the MRCI dipole moment calculation, the $|3_{03}\rangle$ and the $|3_{12}1\rangle$ are overlapping at about 900 V and the $|3_{13}0\rangle$ and $|3_{12}0\rangle$ peaks are overlapping at about 2.0 kV. The difference in the absolute peak positions between the four different calculations is of the order of several hundred volts between the highest μ_z and the lowest μ_z, which makes a careful calibration of all the parameters involved necessary to distinguish between the four sets of dipole moments. In the calculation a beam stop is assumed which blocks all the molecules flying along the center axis of the hexapole.

The peaks of the various quantum states overlap in the focusing spectrum and recording the ion image at the several peak positions will help to deconvolve the spectrum. Although the parent ion does not have kinetic energy release and consequently its angular distribution cannot be measured, the orientation of the parent molecule is reflected in the angular distribution of the fragments.

All the low field seeking states in CH_2OO are relatively high in energy and their population at molecular beam temperatures of about 5 K might be low. However, due to the degeneracy of the M levels, the $J = 3$ state is still sufficiently occupied. The $|3_{03}\rangle$ state has a population of about 1.7%, the $|3_{13}\rangle$ of about 0.8% and the $|3_{12}\rangle$ of about 0.9%. The $|0_{00}0\rangle$ state has a population of 6.5%. In comparison the $|2_{02}\rangle$ state in formaldehyde has a population of 3.4% and

was easily detected after hexapole focusing [11]. The hexapole focus spectrum shown in Figure 3 is not corrected for the Boltzmann factors. In the experiments by McCarthy et al. and Endo et al. the $|1_{01}\rangle \leftarrow |0_{00}\rangle$ transition could be observed showing that the a low rotational temperature of the CH_2OO molecule can be achieved from a discharge source [17,20]. However, the discharge can make a lot of other fragments which may complicate the direct measurement of the molecular properties or reaction dynamics of CH_2OO. The hexapole technique allows the different rotational states of the CH_2OO molecule to be state selected, helping to eliminate the background in direct measurements.

4. Conclusion

Our simulations show that the in situ generated asymmetric top molecule formaldehyde oxide yields sufficiently separated peaks after hexapole focusing. Comparing an experimentally obtained hexapole focusing spectrum with the simulations could confirm the calculated dipole moments with an accuracy within a few percent. Hexapole focusing of CH_2OO from a photolysis reactor or a discharge source could be combined with photodissociation ion imaging to give quantum state resolved values for the dissociation energy of the formaldehyde oxide molecule, or conceivably with molecular beam scattering measurements to investigate reaction dynamics.

References

[1] K.H. Kramer, R.B. Bernstein, J. Chem. Phys. 42 (1965) 767.
[2] D.H. Parker, R.B. Bernstein, Annu. Rev. Phys. Chem. 40 (1989) 561.
[3] K. Schreel, J. Schleipen, A. Eppink, J.J. ter Meulen, J. Chem. Phys. 99 (1993) 8713.
[4] J.J. Leuken, J. Bulthuis, S. Stolte, J.G. Snijders, Chem. Phys. Lett. 260 (1996) 595.
[5] R.W. Anderson, J. Phys. Chem. A. 101 (1997) 7664.
[6] F. Liu, M. Jin, X. Gao, D. Ding, Chin. Phys. Lett. 23 (2006) 344.
[7] T. Suzuki, H. Katayanagi, S. Nanbu, M. Aoyagi, J. Chem. Phys. 109 (1998) 5778.
[8] M.L. Lipciuc, M.H.M. Janssen, J. Chem. Phys. 126 (2007) 194318.
[9] M.H.M. Janssen, J.M. Teule, D.W. Neyer, D.W. Chandler, S. Stolte, Faraday Discuss. 108 (1997) 435.
[10] F. Liu, M. Jin, D. Ding, Chin. Phys. Lett. 23 (2006) 1165.
[11] T.D. Hain, R.M. Moision, T.J. Curtiss, J. Phys. Chem. A 111 (1999) 6797.
[12] D.C. Che, F. Palazzetti, Y. Okuno, V. Aguilanti, T. Kasai, J. Phys. Chem. A 114 (2010) 3280.
[13] R. Criegee, Angew. Chem. Int. Ed. Engl. 14 (1975) 745.
[14] O. Welz, J.D. Savee, D.L. Osborn, S.S. Vasu, C.J. Percival, D.E. Shallcross, C.A. Taatjes, Science 335 (2012) 204.
[15] J.M. Beames, F. Liu, L. Lu, M.I. Lester, J. Am. Chem. Soc. 134 (2012) 20045.
[16] J.H. Lehman, H. Li, J.M. Beames, M.I. Lester, J. Chem. Phys. 139 (2013) 141103.
[17] M.C. McCarthy, L. Cheng, K.N. Crabtree, J. Oscar Martinez, T.L. Nguyen, C.C. Womack, J.F. Stanton, J. Phys. Chem. Lett. 4 (2013) 4133.
[18] Y.-T. Su, Y.-H. Huang, H.A. Witek, Y.-P. Lee, Science 340 (2013) 174.
[19] M.T. Nguyen, T.L. Nguyen, V.T. Ngan, H.M.T. Nguyen, Chem. Phys. Lett. 448 (2007) 183.
[20] M. Nakajima, Y. Endo, J. Chem. Phys. 139 (2013) 01103.
[21] J. Řezáč, P. Hobza, J. Chem. Theory Comput. 9 (2013) 2151.
[22] H.-J. Werner, P.J. Knowles, J. Chem. Phys. 82 (1985) 5053.
[23] H.-J. Werner, P.J. Knowles, J. Chem. Phys. 89 (1988) 5803.
[24] C. Hampel, K. Peterson, H.-J. Werner, Chem. Phys. Lett. 190 (1992) 1.
[25] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
[26] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6769.
[27] T. Helgaker, W. Klopper, H. Koch, J. Noga, J. Chem. Phys. 106 (1997) 9639.
[28] H.-J. Werner, P.J. Knowles, G. Knizia, F.R. Manby, M. Schtz, WIREs Comput. Mol. Sci. 2 (2012) 242.
[29] H.-J. Werner, P.J. Knowles, G. Knizia, F.R. Manby, M. Schtz, et al., MOLPRO, version 2012.1, a package of ab-initio programs, 2012, see <http://www.molpro.net>.
[30] J. Bulthuis, J. Möller, H.J. Loesch, J. Phys. Chem. A 101 (1997) 7684.
[31] R.N. Zare, Angular Momentum, Wiley, New York, 1988.
[32] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, Numerical Recipes, Cambridge University Press, New York, 1990.
[33] H. Ohoyama, T. Ogawa, T. Kasai, J. Phys. Chem. 99 (1995) 13606.