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Tracer correlations in the northern high latitude lowermost stratosphere: Influence of cross-tropopause mass exchange

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Abstract. We present an analysis of trace gas correlations in the lowermost stratosphere. In-situ aircraft measurements of CO, N_2O, NO_y and O_3, obtained during the STREAM 1997 winter campaign, have been used to investigate the role of cross-tropopause mass exchange on tracer-tracer relations. At altitudes several kilometers above the local tropopause, undisturbed stratospheric air was found with NO_y/NO_y* ratios close to unity, NO_y/O_3 about 0.003 - 0.006 and CO mixing ratios as low as 20 ppbv (NO_y* is a proxy for total reactive nitrogen derived from NO_y-N_2O relations measured in the stratosphere). Mixing of tropospheric air into the lowermost stratosphere has been identified by enhanced ratios of NO_y/NO_y* and NO_y/O_3, and from scatter plots of CO versus O_3. The enhanced NO_y/O_3 ratio in the lowermost stratospheric mixing zone points to a reduced efficiency of O_3 formation from aircraft NO_x emissions.

Introduction

In recent years analysis of simultaneous in-situ measurements of stratospheric mixing ratios of NO_y, O_3 and N_2O have revealed simple, compact and nearly linear tracer-tracer relations among these species [e.g. *Murphy et al.*, 1993; *Weinheimer et al.*, 1993; *Fahey et al.*, 1996; *Keim et al.*, 1997; *Singh et al.*, 1997]. The observed anti-correlation between NO_y and N_2O is the most prominent example. Other examples are the positive correlation between NO_y and O_3 and the negative correlation between O_3 and N_2O. *Plumb and Ko* [1992] have shown that compact relations occur among tracers of which chemical lifetimes are long compared to transport and mixing processes. Nevertheless, in-situ measurements of NO_y, O_3 and N_2O onboard the NASA DC-8 [*Weinheimer et al.*, 1993; *Singh et al.*, 1997], the Dutch Cessna Citation II [*Bregman et al.*, 1995; *Fischer et al.*, 1997; *Schneider et al.*, 1999] and the German Falcon [*Schneider et al.*, 1999] revealed that compact relations among these species can also be found in the lowermost stratosphere, a transition region between the local tropopause and the 380 K potential temperature (Θ) level, the approximate height of the tropical tropopause [*Holton et al.*, 1995]. In general, trace gas mixing ratios in the lowermost stratosphere are a mixture of aged stratospheric air descending from the lower stratosphere and recent injections of tropospheric air. Extratropical cross-tropopause transport in mid-latitudes is either due to convection [*Poulida et al.*, 1996; *Ström et al.*, 1999] or isentropic transport across the tropopause in the vicinity of tropopause breaks associated with the subtropical and the polar front jet streams, resulting in a mixing layer extending well above the local tropopause [*Hoerling et al.*, 1993; *Lelieveld et al.*, 1997]. Therefore, tracer-tracer relationships in this mixing layer are expected to deviate significantly from those observed in the lower stratosphere.

In the present study we compare tracer-tracer relations obtained during the STREAM (Stratosphere Troposphere Experiment by Aircraft Measurements) 1997 winter campaign with ER-2 and DC-8 data to investigate the influence of isentropic cross-tropopause transport in the vicinity of the polar front jet stream during late winter on these relations.

Measurements

Simultaneous in-situ measurements of NO_y, N_2O, CO and O_3 were carried out in the lowermost stratosphere in March 1997. Four measurement flights were conducted from Kiruna airport in Sweden (68°N, 20°E) with a Cessna Citation II jet aircraft, up to a maximum altitude of 12.5 km. An area extending from 2°E to 30°E and 68°N to 78°N was investigated between March 3rd and March 25th.

Tunable Diode Laser Absorption Spectroscopy (TDLAS) was used for the evaluation of N_2O and CO mixing ratios with a time resolution of 1 sec [*Wienhold et al.*, 1998]. The measurement precision has been deduced from the reproducibility of the in-flight calibrations, which is ± 2 % on average for both species at the 3 σ-level (5 sec time resolution). The uncertainty of the calibration gas standards is ± 2.8 %. The noise level for 5 sec averages is of the order of ± 4.5 ppbv for CO and ± 2.3 ppbv for N_2O, respectively.

The NO_y measurement is based on the gold catalyzed reduction of the NO_y species NO_2, NO_3, N_2O_5, HONO, HNO_3, HO_2NO_2, $ClONO_2$, and PAN to NO in the presence of CO (0.3 %) in a heated Au-tube (300°C) with subsequent NO detection by a chemiluminescence detector (ECO-Physics CLD 770 AL pptv) with a time resolution of 1 sec [*Fischer et al.*, 1997]. The

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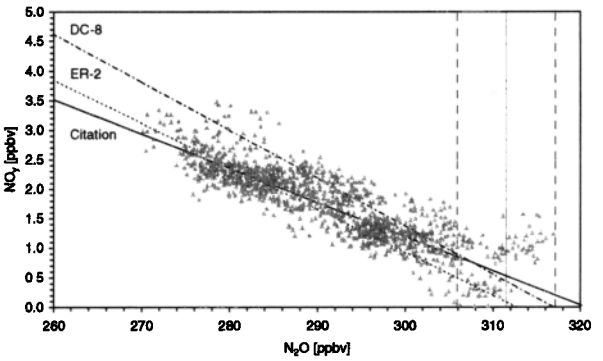

Figure1: Scatter plot of NO_y vs. N_2O. Linear correlations obtained during the STRAT mission in January 1996 with the ER-2 (NO_y = (312.7 – N_2O) x 0.073 [*Keim et al.*, 1997]) and during the PEM-West B campaign in spring 1994 with the DC-8 (NO_y = (316.9 – N_2O) x 0.081 [*Singh et al.*, 1997]). A reduced major axis least square fit to the STREAM data yields NO_y = [(323.8 ± 4.6) – N_2O] x (0.057 ± 0.001). The vertical lines represent the upper tropospheric mixing ratio of N_2O [311.5 ± 5.6 ppbv (standard deviation at the 2σ-level)].

precision of the NO_y measurement is estimated from the standard deviation of in-flight NO_2 calibrations to be ± 10 % (1σ). The accuracy, which is determined by the uncertainty of the calibration gas standards and the conversion efficiencies for different NO_y species not determined in the field, is of the order of ± 15 % (1σ) plus precision.

A modified pressure independent chemiluminescence monitor (Bendix 8002) based on the reaction with ethylene was used to measure ozone at 1 Hz time resolution, a precision of 2% and an accuracy of 10% [*Bregman et al.*, 1995].

Results and Discussion

The STREAM data (30 sec averages from the four STREAM flights in 1997) were obtained in the lowermost stratosphere between the local tropopause located at Θ-levels between 285 and 300 K (400-300 hPa) and maximum potential temperature of 355 K (200 hPa). Figure 1 shows a scatter plot of NO_y vs. N_2O. The STREAM 97 data are grouped around linear correlation functions calculated from ER-2 data, which were obtained during the STRAT mission in January 1996 [*Keim et al.*, 1997] and from DC-8 data obtained during the PEM-West B campaign in spring 1994 [*Singh et al.*, 1997]. Considering the altitude range of the aircraft involved, the STREAM data (8.5–13 km) are intermediate between the DC-8 (8-12 km) and the ER-2 (15-21 km) data. Application of a least square fit, taking into account errors in both the x and y variables of the STREAM data, yields NO_y = [(320.6 ± 1.0) – N_2O] x (0.058 ± 0.002)] for N_2O values less than 300 ppbv. Compared to correlation functions obtained during the most recent missions by the DC-8 (PEM-West (B) 1994 [*Singh et al., 1997*]) and the ER-2 (STRAT 1996 [*Keim et al., 1997*]) the slope of the regression calculated from the STREAM data is significantly smaller by approximately 10 – 25 %, while the intercept is significantly higher (Table 1). For N_2O values between 270 and 300 ppbv the STREAM NO_y-N_2O relationship is in-between those obtained from DC-8 and ER-2 data, being closer to the DC-8 values at higher N_2O mixing ratios and closer to the ER-2 values at lower N_2O mixing ratios (Fig. 1).

If we assume that the ER-2 relation shown in Fig. 1 is representative for lower stratospheric air, while the DC-8 data represent air close to the tropopause, the STREAM data can be interpreted as a combination of undisturbed stratospheric air, descending from the lower stratosphere, and tropospheric air of mid- and high latitude origin. To differentiate between both transport pathways a scatter plot of O_3 vs. CO can be used (Fig. 2). The mixing ratios of both species exhibit strong gradients at the tropopause, with high CO (low O_3) values in the troposphere and low CO (high O_3) values in the stratosphere. In the troposphere, which can be identified by CO mixing ratios in excess of 100 ppbv, the O_3 mixing ratio is nearly constant at approximately 60 ppbv (red points in Fig. 2). Here the CO-O_3 regression shows no correlation at all (red trend line in Fig. 2). A negative slope between CO and O_3 is obtained for CO mixing ratios between 15 ppbv and approximately 30 ppbv (blue points and line in Fig. 2), mixing ratios typical for aged stratospheric air [*Herman et al.*, 1999]. Cross-tropopause mixing can be identified by deviations from the L-shape formed by the two trend lines in Fig. 2 (green dots). Mixing of tropospheric and stratospheric air masses results in CO mixing ratios between approx. 30 and 100 ppbv. These are also typical values for CO observed onboard the DC-8 in the lowermost stratosphere up to 4 km above the local tropopause [*Weinheimer et al.*, 1994; *Singh et al.*, 1997]. In the following analysis we use the same color coding to differentiate between tropospheric (red) and undisturbed stratospheric air (blue), and a mixture of these air masses (green).

In Fig. 3 the ratio of NO_y and NO_y*, the latter a proxy for the available stratospheric NO_y calculated from N_2O, using the relation from the ER-2 data obtained during the STRAT mission in January 1996 (NO_y*(ER-2) = (312.7 – N_2O) x 0.073) [*Keim et al.*, 1997], is plotted as a function of N_2O. For N_2O values less than approx. 285 ppbv, i.e. for the majority of the blue dots, this ratio is very close to unity (dashed line), while the ratio increases in the vicinity of the tropopause (290 ppbv ≤ N_2O ≤ 305 ppbv).

Similar characteristics can be found in a scatter plot of the NO_y/O_3 ratio as a function of N_2O (Fig. 4). Earlier studies have shown that the NO_y/O_3 ratio is approximately 0.003 in the extra-tropical stratosphere at 10 – 18 km [*Murphy et al.*, 1993; *Weinheimer et al.*, 1993; *Fahey et al.*, 1996], while measurements at lower altitudes, in particular at high latitudes, indicate higher ratios, roughly 0.004 – 0.006 [*Murphy et al.*, 1993; *Weinheimer et al.*, 1993; 1994]. Upper tropospheric ratios of NO_y/O_3 were found to be much higher (~ 0.008 – 0.016) [*Weinheimer et al.*, 1993]. Figure 4 indicates that for the present data set the NO_y/O_3 ratio is of the order of 0.003 to 0.005 for N_2O mixing ratios below 295 ppbv (blue dots), while increasing values are observed in the mixing layer above the tropopause (green dots). Upper tropospheric values are approximately 0.01 to 0.03.

A scatter plot of NO_y/NO_y* versus NO_y/O_3 normalized by a factor 0.004, a representative stratospheric value for the latter ratio, indicates a significant correlation (R^2=0.4, N= 1229) (not shown). A trend analysis yields a linear correlation with a slope of ΔNOy/NOy* = 0.94 x Δ(NOy/O3)/0.004. Therefore, the observed deviation of NO_y/NO_y* from unity and the simultaneous

Table 1: Measured NO_y-N_2O correlation in the northern hemisphere*

Mission	Aircraft	Period	Slope	Intercept
AASE II	ER-2	91/92	-0.064	323.4
ASHOE/MAESA	ER-2	Apr 94	-0.069±0.001	314.5±2.8
ASHOE/MAESA	ER-2	Oct 94	-0.068±0.001	317.9±1.2
STRAT	ER-2	Oct 95	-0.068±0.0002	318.4±0.9
STRAT	ER-2	Jan 96	-0.073±0.0002	312.7±0.7
AASE II	DC-8	Jan-Mar 92	-0.078	319.0
AASE II	DC-8	Feb 92 only	-0.066	321.0
PEM-West (B)	DC-8	Feb/Mar 94	-0.081	316.9
STREAM	Cessna	Mar 97	-0.058±0.002	320.6±1.0

*adapted from *Keim et al.* [1997], *Weinheimer et al.* [1993] and *Singh et al.* [1997].

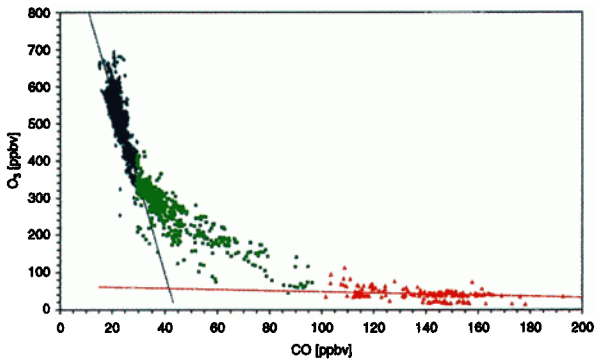

Figure 2: Scatter plot of O_3 versus CO. Data points are color-coded according to their origin from the unperturbed stratosphere (blue) or the troposphere (red). Mixing between stratospheric and tropospheric air-masses is indicated by green data points. Regression lines for tropospheric and stratospheric relations among these species are indicated in the color code of the air mass origin.

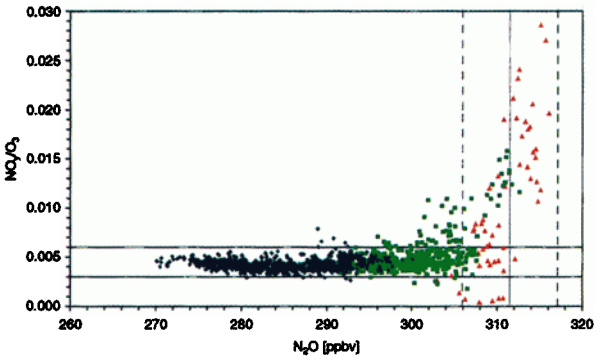

Figure 4: Scatter plot of NO_y/O_3 versus N_2O. The individual data points are color-coded according to the classification in Fig. 2. The vertical lines indicate the mean mixing ratio of N_2O in the upper troposphere and its standard deviation at the 2σ-level.

enhancements of the NO_y/O_3 ratio indicate an excess of NO_y in the mixing layer compared to lower stratospheric NO_y mixing ratios. The prime source of NO_y in the stratosphere is photochemical destruction of N_2O, which largely takes place in the tropical middle stratosphere. An additional source of reactive nitrogen in particular in the lowermost stratosphere is associated with aircraft exhausts. The mean increase in NO_y concentrations due to aircraft emissions in the tropopause region of northern mid-latitudes has been estimated at about 10 – 50 % [*Brasseur et al.*, 1998]. In addition, enhancements of NO_y in the lowermost stratosphere can be due to vertical redistribution of HNO_3 by sedimentation and evaporation of PSC particles [*Hübler et al.*, 1990; *Fischer et al.*, 1997], oversampling of NO_y due to particulate NO_y [*Fahey et al.*, 1989] or mixing with the extratropical troposphere. In the present case oversampling can be excluded, since the temperatures at flight level were well above the existence temperature of PSCs. Redistribution of reactive nitrogen due to particle sedimentation is also unlikely, since the enhancements in NO_y/NO_y* are associated with increased CO mixing ratios, indicating that the "excess" NO_y originates from the troposphere. Individual case studies relying on back-trajectory calculations indeed indicate that isentropic cross-tropopause transport is most likely responsible for the enhanced NO_y in this mixing layer.

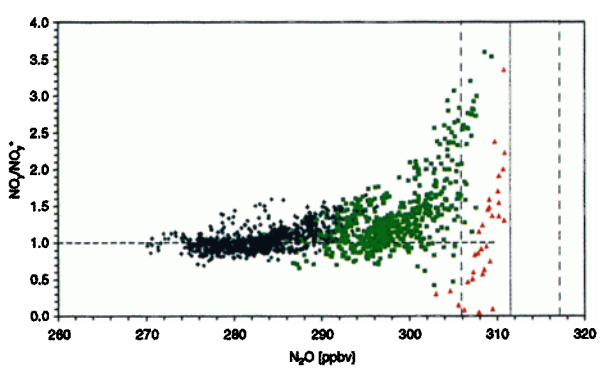

Figure 3: Scatter plot of NO_y/NO_y* versus N_2O. The individual data points are color-coded according to the classification in Fig. 2. The vertical lines indicate the mean mixing ratio of N_2O in the upper troposphere and its standard deviation at the 2σ-level. The horizontal dashed line is the NO_y/NO_y* ratio in unperturbed stratospheric air.

NO_y mixing ratios in the upper troposphere during STREAM-97 were of the order of 0.7 ppbv, in good agreement with earlier observations [*Weinheimer et al.*, 1994], however, too low to explain the large enhancements of NO_y/NO_y* in the lowermost stratospheric mixing layer (Fig. 3). Exchange across the tropopause due to convection [*Poulida et al.*, 1996; *Ström et al.*, 1999] or gravity wave induced cross-tropopause transport [*Langford et al.*, 1996; *Schilling et al.* 1999] might contribute to the few data points with NO_y/NO_y* < 1 between 300 and 305 ppbv N_2O in Fig. 3. Higher mixing ratios of NO_y up to 2 ppbv can be found in the upper troposphere in mid-latitudes [*Klemm et al.*, 1998], indicating that cross-tropopause transport associated with tropopause folds at the jet streams in middle and subtropical latitudes [*Hoerling et al.*, 1993] most probably has caused the enhancements of both NO_y and CO in the mixing layer in the middle and high latitude northern lowermost stratosphere.

The cross-tropopause mixing has consequences for photochemical O_3 formation, for example from aircraft NO_x emissions. Model calculations have shown that the O_3 formation per unit NO_x decreases at increasing NO_y/O_3 ratios [*Bregman et al.*, 1997; *Brasseur et al.*, 1998]. *Bregman et al.* [1997] used a chemical model to illustrate that the photochemical destruction of nitrogen reservoir species (mainly HNO_3) largely determines the availability of NO_x in the lowermost stratosphere. Sensitivity studies, applying additional NO_x perturbations from aircraft, showed that the O_3 production efficiency per NO_x may be smaller than previously assumed, under conditions with relatively high NO_y/O_3 ratios. In addition to NO_y pollution transport from the troposphere, dilution of lower stratospheric O_3 by O_3-depleted tropospheric air enhances NO_y/O_3 ratios. Therefore, cross-tropopause mixing reduces the sensitivity of O_3 photochemistry to NO_x perturbations from aircraft exhausts.

Conclusions

Trace gas measurements of CO, N_2O, NO_y, and O_3 in the lower stratosphere in the winter 1997 at altitudes between 8 and 13.5 km confirm the existence of a mixing layer 2–3 km above the local tropopause which strongly influences tracer relationships in the lowermost stratosphere. Above this layer observed trace gas concentrations and ratios between various tracers exhibit signatures typical of undisturbed lower stratospheric air, in agreement with ER-2 observations previously obtained at higher altitudes (15-21 km). In particular very low CO mixing ratios of about 20 ppbv indicate that these air masses are

dominated by diabatic descent from higher layers of the stratosphere. Cross-tropopause transports results in a mixing layer, characterized by elevated mixing ratios of CO and NO_y, and significantly enhanced NO_y/O_3 ratios. As a consequence, cross-tropopause mixing reduces the efficiency of pollutant O_3 formation from aircraft NO_x emissions in the lowermost stratosphere.

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References:

Bregman, A., et al., Aircraft measurements of O_3, HNO_3, and N_2O in the winter Arctic lower stratosphere during the Stratosphere-Troposphere Experiment by Aircraft Measurements (STREAM) 1, *J. Geophys. Res., 100*, 11245-11260, 1995.

Bregman, A. et al., In situ trace gas and particle measurements in the summer lower stratosphere during STREAM II: Implications for O_3 production, *J. Atmos. Chem., 26*, 275-310, 1997.

Brasseur, G.P., et al., European scientific assessment of the atmospheric effects of aircraft emissions, *Atmos. Environm., 32*, 2329-2418, 1998.

Fahey, D.W., et al., In situ measurements of total reactive nitrogen, total water, and aerosol in a polar stratospheric cloud in the Antarctic, *J. Geophys. Res., 94*, 11299-11315, 1989.

Fahey, D.W., et al., In situ observations of NO_y, O_3, and the NO_y/O_3 ratio in the lower stratosphere, *Geophys. Res. Lett., 23*, 1653-1656, 1996.

Fischer, H., et al., Observations of high concentrations of total reactive nitrogen (NO_y) and nitric acid (HNO_3) in the lower Arctic stratosphere during the Stratosphere-Troposphere Experiments by Aircraft Measurements (STREAM) II campaign in February 1995, *J. Geophys. Res., 102*, 23559-23571, 1997.

Herman, R.L., et al., Measurements of CO in the upper troposphere and lower stratosphere, *Chemosphere – Global Change Science, 1*, 173-184, 1999.

Hoerling, M.P., T.K. Schaack, and A.J. Lenzen, A global analysis of stratospheric-tropospheric exchange during northern winter, *Mon. Wea. Rev., 121*, 162-172, 1993.

Holton, J.R., et al., Stratosphere-Troposphere Exchange, *Rev. of Geophys, 33*, 403-439, 1995.

Hübler, G., et al., Redistribution of reactive odd nitrogen in the lower Arctic stratosphere, *Geophys. Res. Lett., 17*, 453-456, 1990.

Keim, E.R., et al., Measurements of the NO_y-N_2O correlation in the lower stratosphere: Latitudinal and seasonal changes and model comparisons, *J. Geophys. Res., 102*, 13193-13212, 1997.

Klemm, O., W.R. Stockwell, H. Schlager, and H. Ziereis, Measurements of nitrogen oxides in the northeast Atlantic flight corridor, *J. Geophys. Res., 103*, 31217-31229, 1998.

Lamarque, J.-F., A.O. Langford, and M.H. Proffitt, Cross-tropopause mixing of ozone through gravity wave breaking: Observations and modeling, *J. Geophys. Res., 101*, 22969-22976, 1996.

Lelieveld, J., et al., Chemical perturbation of the lowermost stratosphere through exchange with the troposphere, *Geophys. Res. Lett., 24*, 603-606, 1997.

Murphy, D.M., et al., Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res., 98*, 8751-8773, 1993.

Plumb, R.A., and KO, M.K.W., Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res., 97*, 10145-10156, 1992.

Poulida, O., R.R. Dickerson, and A. Heymsfield, Stratosphere-troposphere exchange in a midlatitude mesoscale convective complex: 1. Observations, *J. Geophys. Res., 101* 6823-6836, 1996.

Schilling, T., F.-J. Lübken, F.G. Wienhold, P. Hoor, and H. Fischer, TDLAS trace gas measurements within mountain waves over northern Scandinavia during the POLSTAR Campaign in early 1997, *Geophys. Res. Lett., 26*, 303-306, 1999.

Schneider, J., et al., The temporal evolution of the ratio HNO_3/NOy in the Arctic lower stratosphere from January to March 1997, *Geophys. Res. Lett., 26*, 1125-1128, 1999.

Singh, H.B., et al., Trace chemical measurements from the northern midlatitude lowermost stratosphere in the early spring: Distributions, correlations, and fate, *Geophys. Res. Lett., 24*, 127-130, 1997.

Ström, J., H. Fischer, J. Lelieveld, and F. Schröder, In.situ measurements of microphysical properties and trace gases in two cumulonimbus anvils over western Europe, *J. Geophys. Res., 104*, 12221-12226, 1999.

Weinheimer, A.J., et al., Stratospheric NO_y measurements on the NASA DC-8 during AASE-II, *Geophys. Res. Lett., 20*, 2563-2566, 1993

Weinheimer, A.J., et al., Meridional distribution of NO_x, NO_y, and other species in the lower stratosphere and upper troposphere during AASE II, *Geophys. Res. Lett., 21*, 2583-2586, 1994.

Wienhold, F.G., et al., TRISTAR – a tracer in-situ TDLAS for atmospheric research, *Appl. Phys., B 67*, 411-417, 1998.

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