Host Spin-Lattice Relaxation Narrowing in $Pr_2Co_3(NO_3)_{12} \cdot 24\,H_2O : Mn^{2+}, Gd^{3+}$ Single Crystals *

Vimal Kumar Jain

Department of Physics, M. D. University, Rohtak-124001 (Haryana), India

Z. Naturforsch. **35a**, 1308–1312 (1980); received January 7, 1980

Electron paramagnetic resonance of Mn^{2+} and Gd^{3+} in single crystals of $Pr_2Co_3(NO_3)_{12} \cdot 24\,H_2O$ has been studied at X-band at 305 and 77 K. Mn^{2+} substitutes at two types of Co^{2+} sites whereas Gd^3 substitutes at the single type of Pr^{3+} site in the lattice. The spin-Hamiltonian parameters have been evaluated. Observation of resolved Mn^{2+} and Gd^{3+} spectra at 305 K and their broadening on lowering the temperature are discussed in terms of host spin-lattice relaxation narrowing.

1. Introduction

The hydrated double nitrates of the rare earth elements form an interesting isomorphous series of salts for electron paramagnetic resonance (EPR) studies [1–15]. Their general formula is $M_2'''M_3''(NO_3)_{12} \cdot 24\,H_2O$, where M''' is a trivalent cation (Bi or an ion of the 4f group) and M'' is a divalent cation (Zn, Mg or an ion of the 3d group). We have previously reported the EPR of Mn^{2+} and Gd^{3+} in some of the double nitrates [13–15] at room temperature and at liquid nitrogen temperature. These studies indicated that Sm^{3+}, Pr^{3+}, and Nd^{3+} behave virtually as diamagnetic ions with respect to Mn^{2+} and Gd^{3+} at least down to liquid nitrogen temperature. Gerkin and Thorsell [16] have previously shown that the ethyl sulfate nonahydrates of Pr^{3+} and Sm^{3+} behave virtually as diamagnetic systems with respect to Gd^{3+} down to 77 K as regards linewidths whereas Nd ethyl sulfate nonahydrate behaves as a paramagnetic system. But the $g_{\|}$ of Gd^{3+} in ethyl sulfate nonahydrates of Pr, Sm, and Nd has the same value, within the experimental errors, to that observed for Gd^{3+} in diamagnetic lanthanum ethyl sulfate nonahydrate. This paper reports the EPR of Mn^{2+} and Gd^{3+} in paramagnetic $Pr_2Co_3(NO_3)_{12} \cdot 24\,H_2O$ (PCN) single crystals at 305 and 77 K. Misumi et al. [7] studied the EPR of Gd^{3+} in various double nitrates (including Co salts) at room temperature and determined the various spin-Hamiltonian parameters. Their main interest was to correlate the zero-field splitting parameter with the ionic radii. They have extended their EPR studies of Gd^{3+} in double nitrates down to liquid He temperature only for $La_2M_3''(NO_3)_{12} \cdot 24\,H_2O$ (M'' = Mg, Zn). They have not reported low temperature EPR measurements in Co salts. The EPR of Mn^{2+} in PCN has not been reported earlier. The present study has been undertaken in order to observe the effect of Co^{2+} on the EPR spectra of impurity ions in PCN and thus to study host spin-lattice relaxation narrowing.

2. Crystal Structure

The crystal structure of $Ce_2Mg_3(NO_3)_{12} \cdot 24\,H_2O$ (CMN), which is isomorphous to PCN [5, 9], has been determined by Zalkin et al. [17]. The primitive cell of CMN contains one formula unit and is rhombohedral with lattice constants $a = 13.165$ Å and $\alpha = 49.37°$. The space group is $R\bar{3}$. The unit cell contains three divalent ions situated at two different lattice sites. One of them occupies the site with the point symmetry C_{3i} (Y site or site I) and the other two occupy lattice sites with the point symmetry C_3 (X site or site II). Each X site has a nearest neighbour (nn) X site, 4.99 Å away along the c (trigonal) axis, and three nn Y sites, 7.14 Å away and at an angle of 62.7° from the c axis [6]. The trivalent ion is found at a site of C_3 point symmetry and the rest of the atoms are in the general positions of the space graup. The nearest trivalent neighbours are 3 at 8.50 Å and 3 at 8.59 Å [17]. The nearest divalent neighbours of

* Revised Version was received October 16, 1980.

Reprint requests to Dr. V. K. Jain, Department of Physics, M. D. University, Rohtak-124001, Haryana, India.

0340-4811 / 80 / 1200-1308 $ 01.00/0. — Please order a reprint rather than making your own copy.

trivalent ions are 1 at 6.17 Å, 3 each at 6.36, 6.98 and 8.31 Å, and 1 at 8.64 Å [17]. The divalent ions are surrounded by six water molecules forming nearly regular octahedral $[M''(H_2O)_6]^{2+}$ complexes. Each trivalent ion is coordinated with 12 oxygens belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron.

3. Experimental

Single crystals of PCN doped with Mn^{2+} and Gd^{3+} were grown at room temperature by slow evaporation of aqueous solutions of $Pr(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ mixed in stoichiometric ratios. Mn^{2+} and Gd^{3+} were introduced into the host lattice by adding a small amount (0.5 — 1 % by weight) of manganese and gadolinium nitrates. The double nitrates grow in flat hexagonal plates, the plane of which is perpendicular to the trigonal axis. Details of the experimental set up for recording the EPR spectra are given in [18].

4. Results and Discussion

4.1. Mn^{2+}

In double nitrates the Mn^{2+} occupy two different divalent cation sites with their z axes along the trigonal (c) axis of the crystal [2, 3, 12, 13, 19]. Figure 1 shows the EPR spectrum of PCN : Mn^{2+} with magnetic field parallel to the c axis. Magnetic field measurements have been made only for the Mn^{2+} complex having a large zero-field splitting (Y site). No measurement could be made for the Mn^{2+} complex having a small zero-field splitting (X site) since various fine structure groups could not be distinguished. Further, for the Y site, measurements could be made only for $M = \pm 5/2 \rightarrow \pm 3/2$ transitions because the inner transitions $M = \pm 3/2 \rightarrow \pm 1/2$ and $M = +1/2 \rightarrow -1/2$ are completely broadened out. The following discussion pertains only to the Y site. The spectra of the Y site observed at 305 K have been analysed using the spin-Hamiltonian appropriate for Mn^{2+} in a

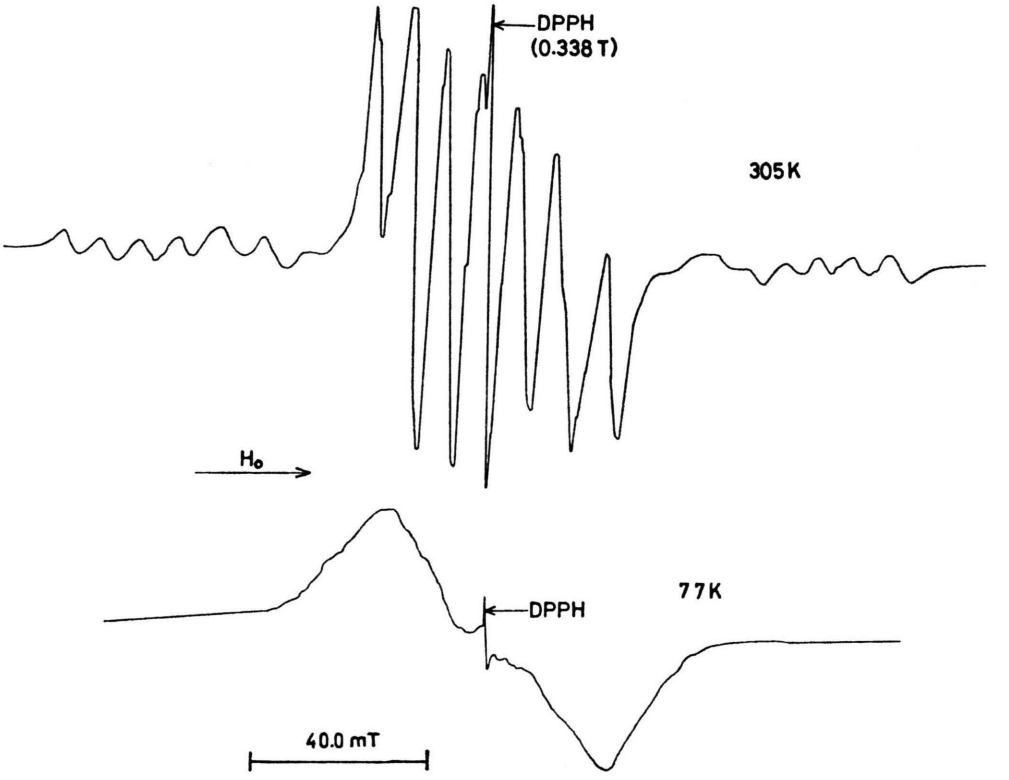

Fig. 1. The EPR spectra of $Pr_2Co_3(NO_3)_{12} \cdot 24H_2O$:$Mn^{2+}$ single crystals at 305 and 77 K for $H_0 \| z$ axis at X-band frequencies (9.5 GHz).

trigonal crystalline field [12, 13, 20]. The spin-Hamiltonian parameters of Mn^{2+} (at Y site) in PCN at 305 K (in units of 10^{-4} cm^{-1}) are: $b_2^0 = -184.3$, $[2(b_4^0)_c - 3b_4^0] = 6.4$, $g_\parallel = 2.0086$, $g_\perp = 2.0070$, $A_\parallel = -88.9$, $A_\perp = -89.2$. The signs of the parameters are only relative and have been determined from the observed second order hyperfine shift, assuming $A_\parallel$ to be negative. The parameters are of the same order as observed for Mn^{2+} in $Pr_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (PMN) [12] and $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$ (PZN) [13].

The general features of the Mn^{2+} spectra in PCN are similar to those observed in PMN and PZN. However, several differences are observed:

(i) The widths of the Mn^{2+} resonance lines associated with various fine structure groups in PCN show an unusual variation. The linewidths of various fine structure groups for H_0 parallel to the z axis increase on going from the $M = \pm 5/2 \rightarrow \pm 3/2$ towards the $M = +1/2 \rightarrow -1/2$ transition. In fact, the widths of the $M = \pm 3/2 \rightarrow \pm 1/2$ and $M = +1/2 \rightarrow -1/2$ groups were so large that the signals were completely broadened out and only $M = \pm 5/2 \rightarrow \pm 3/2$ were resolved. However, in PMN and PZN no unusual behaviour of linewidths is observed and the spectra are well resolved.

(ii) At 305 K the linewidths of the Mn^{2+} spectra in PCN (which is ≈ 5.5 mT for the $M = \pm 5/2 \rightarrow \pm 3/2$ transition) are larger than those in PMN and in PZN (which are ≈ 1.1 mT) [13].

(iii) The widths of all the Mn^{2+} resonance lines increase on lowering the temperature of the crystal. The Mn^{2+} spectra are completely broadened out and show a single band at 77 K. On raising the temperature again, the resolved spectra reappear, indicating that the smearing out of the spectra at 77 K is due to increased linewidths on lowering the temperature. As the spectrum was completely unresolved at 77 K, therefore, no determination of the spin-Hamiltonian parameters could be made in this case. These observations are in contrast with those of Mn^{2+} in PMN and PZN where no appreciable broadening is observed at 77 K.

4.2. Gd^{3+}

The EPR spectrum consists of a single set of seven lines with the z axis parallel to the c axis. Figure 2 shows the EPR spectra of PCN : Gd^{3+} with H_0 parallel to the z axis at 305 and 77 K. The subsidiary maxima (x axis) occur when the external magnetic field is perpendicular to the c axis. However, when the field is in the plane perpendicular to the c axis, all the observed fine structure transitions do not attain an extremum. The departure from the perpendicular direction is as much as $\approx 8°$, and the corresponding change in the field position

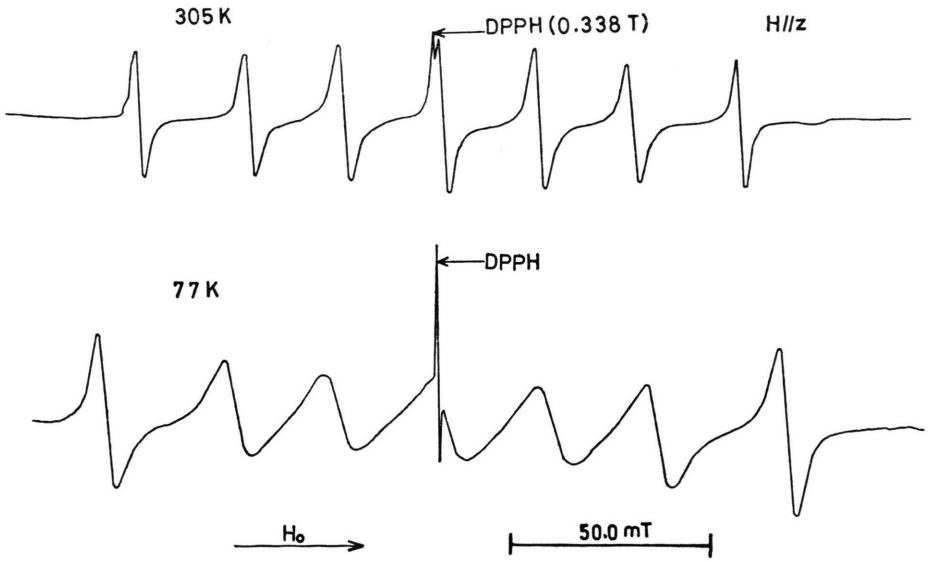

Fig. 2. The EPR spectra of $Pr_2Co_3(NO_3)_{12} \cdot 24H_2O$: Gd^{3+} single crystals at 305 and 77 K for $H_0 \| z$ axis at X-band frequencies (9.5 GHz).

is ≈ 1.2 mT, which is more than the experimental error. This anomalous angular variation of fine structure transition in the plane perpendicular to the c axis has been previously observed in other hydrated double nitrates [5, 9, 14]. The spectrum shows trigonal symmetry about the c axis.

The spectrum has been analysed using the spin-Hamiltonian appropriate for Gd^{3+} in a trigonal crystalline field [5]. The parameters at 305 and 77 K are given in Table 1. The signs of the parameter b_n^m given in this table are only relative and have been determined assuming b_2^0 to be positive. The parameters b_6^6 and $g_\perp$ are not quoted because of the anomalous angular variation of the fine structure transitions in the plane perpendicular to the z axis. The parameters of Gd^{3+} in PCN are of the same order as observed for Gd^{3+} in PMN and PZN.

The observed behaviour of the Gd^{3+} spectra in PCN deviates from the PMN(PZN) : Gd^{3+} spectra in several aspects:

(i) At 305 K the linewidths of the Gd^{3+} spectra in PCN are ≈ 2.8 mT (Table 2) whereas the widths are ≈ 0.8 mT in PMN and PZN at room temperature and at 77 K.

(ii) The linewidths of various fine structure transitions in PCN : Gd^{3+} show an unusual variation (Table 2). For H_0 parallel to the z axis the linewidths increase on going from the $M = \pm 7/2 \rightarrow \pm 5/2$ to the $M = +1/2 \rightarrow -1/2$ transition. The width of all the Gd^{3+} resonance lines increases on lowering the temperatures, and the unusual variation of linewidths becomes prominent at 77 K (Figure 2). The broadening of the central transition and narrowing towards the end of the spectrum is also observed for Gd^{3+} in some rare earth salts [16, 21]. However, so such effect has been observed in PMN and PZN from room temperature to 77 K.

(iii) The values of $g_\parallel$ for Gd^{3+} in PCN (1.990 ± 0.001 at 305 K and 1.987 ± 0.001 at 77 K) show a shift from the value which is observed in the case of PMN ($g_\parallel = 1.9922 \pm 0.0005$ at 300 and 77 K) [14] and PZN ($g_\parallel = 1.9925 \pm 0.0005$ at 298 K and 1.9924 ± 0.0005 at 77 K) [13].

Table 1. Spin-Hamiltonian parameters for Gd^{3+} in $Pr_2Co_3(NO_3)_{12} \cdot 24\,H_2O$ single crystals at 305 and 77 K. All crystal field parameters are in units of 10^{-4} cm^{-1}.

Spin-Hamiltonian parameters	305 K	77 K
b_2^0	115.0 ± 1.0	128.9 ± 1.0
b_4^0	0.65 ± 0.05	1.0 ± 0.05
b_6^0	0.42 ± 0.05	0.47 ± 0.05
$g_\parallel$	1.990 ± 0.001	1.987 ± 0.001

Table 2. Signal widths of Gd^{3+} in $Pr_2Co_3(NO_3)_{12} \cdot 24\,H_2O$ single crystals at 305 and 77 K for H_0 parallel to the z axis.

$M \rightarrow M-1$	Width (mT)	
	305 K	77 K
$7/2 \rightarrow 5/2$	2.37	3.80
$5/2 \rightarrow 3/2$	2.85	7.12
$3/2 \rightarrow 1/2$	2.85	9.02
$1/2 \rightarrow -1/2$	3.32	9.60
$-1/2 \rightarrow -3/2$	3.32	9.00
$-3/2 \rightarrow -5/2$	3.32	6.65
$-5/2 \rightarrow -7/2$	2.60	3.60

The linewidths of Mn^{2+} and Gd^{3+} in PCN can probably be understood on the basis of host spin-lattice relaxation. Mitsuma [22] proposed that fast spin-lattice relaxation of the host can randomly modulate the dipolar and exchange interactions between paramagnetic host and impurity ions, resulting in what is called "host spin-lattice relaxation narrowing" [23]. In PCN, both Pr^{3+} and Co^{2+} are fast relaxing ions. However, it has been shown by Gerkin and Thorsell [16] that Pr ethyl sulfate nonahydrate, a comparably dilute salt, behaves virtually as a diamagnetic host with respect to Gd^{3+} down to 77 K. Similar observations are made for PMN and PZN relative to Mn^{2+} and Gd^{3+} [12—14]. Therefore, the observed linewidth broadening in PCN can not arise from the magnetic interaction between Pr^{3+} and impurities. It can be explained as a result of the interaction between fast relaxing Co^{2+} and impurities. St. John [24] has shown that the requirement stated in motional narrowing theory can be met in the case of Mn^{2+} (and for Gd^{3+}, which is also an S state ion) in cobalt salts at higher temperatures (300 K) and at X-band. Thus the observation of resolved EPR spectra of Mn^{2+} and Gd^{3+} in PCN single crystals can be attributed to the host spin-lattice relaxation narrowing.

To rule out the possibility that the resolved spectrum is due to motional narrowing because of exchange interaction between the host ions, and also to confirm that it is due to host spin-lattice relaxation, measurements have been carried out at 77 K. In the case of exchange narrowing there will be almost no temperature dependence of

impurity linewidths until one goes much below 77 K [23]. For host spin-lattice relaxation narrowing the width of the impurity resonance lines should increase on lowering the temperature, as observed, because the host relaxation time T_1 should increase on lowering the temperature and then it will not be able to average out dipolar interaction as effectively [25]. The line broadening with decreasing temperature has previously been observed in some cobalt [23] and rare earth salts [21, 26].

When the conditions for host spin-lattice relaxation narrowing are met, the spin-lattice relaxation time T_1 can be determined from the impurity linewidths. St. John [24] has given an expression for T_1 (host). From the observed linewidth of Mn^{2+} and Gd^{3+} at 305 K (in PCN), the spin-lattice relaxation time of Co^{2+} in PCN has been estimated using the expression for T_1 [23, 24]. From the Mn^{2+} linewidth, $T_1 = \approx 6 \times 10^{-11}$ sec. and from the Gd^{3+} linewidths, $T_1 = \approx 4 \times 10^{-11}$ sec. As crystal structure data of PCN are not available, in the calculations of T_1 crystallographic data of CMN have been used and the g-factor is taken from the $La_2Mg_3(NO_3)_{12} \cdot 24H_2O : Co^{2+}$ data [6]. The order of T_1 for Co^{2+} in PCN is found to be in agreement with that calculated for other cobalt salts [23].

Gerkin and Thorsell [16], and Saraswat and Upreti [23] explained the unusual variation of the linewidth for different fine structure transitions as probably due to unequal influence of exchange interaction upon various $\Delta M = \pm 1$ transitions of Mn^{2+} and Gd^{3+}. However, in view of the very close $g_{\|}$-shift of Gd^{3+} in the lanthanide ethyl sulfate nonahydrates, comparably dilute salts, found by Gerkin and Rogers [27] as measured and calculated on a pure magnetic dipolar interaction model, it appears that exchange interaction is unimportant for Gd^{3+} in lanthanide ethyl sulfate nonahydrates, where, however, the same behaviour of linewidth is observed in (strongly) paramagnetic cases. Thus, it appears that exchange interaction is unlikely to be the basis of the linewidth variation. The observed $g_{\|}$-shift indicates magnetic interaction between impurity ions (Gd^{3+}) and surrounding Co^{2+} ions. The $g_{\|}$-shift has also been observed previously in other paramagnetic salts [21, 23].

Acknowledgements

The author is thankful to Professor Putcha Venkateswarlu of Indian Institute of Technology Kanpur for providing the experimental facilities for doing this work and to Dr. R. S. Saraswat of Indian Institute of Technology Khargapur for helpful discussions.

[1] R. S. Trenam, Proc. Phys. Soc. **A 66**, 118 (1953).
[2] D. Van Ormondt and T. Thalhammer, Phys. Lett. **14**, 169 (1965).
[3] B. M. Brandt, D. Van Ormondt, and T. Thalhammer, Phys. Lett. **19**, 549 (1966).
[4] J. W. Culvahouse, W. Unruch, and R. C. Sapp, Phys. Rev. **121**, 1370 (1961).
[5] H. A. Buckmaster, J. C. Dering, and D. J. I. Fry, J. Phys. C **1**, 599 (1968).
[6] J. W. Culvahouse and D. P. Schink, Phys. Rev. **187**, 671 (1969).
[7] S. Misumi, T. Isobe, and T. Higa, Nippon Kagaku Kaishi **11**, 2039 (1973); **10**, 1829 (1974); **5**, 743 (1975).
[8] M. L. Meil'man, Soviet Physics Solid State **14**, 2612 (1973).
[9] M. L. Meil'man and M. I. Samoilovich, Soviet Physics Crystallogr. **20**, 200 (1975).
[10] R. T. Dixon and J. W. Culvahouse, Phys. Rev. **B 14**, 1830 (1976).
[11] J. W. Culvahouse and C. L. Francis, J. Chem. Phys. **66**, 1079 (1977).
[12] V. K. Jain and T. M. Srinivasan, Z. Naturforsch. **32a**, 665 (1977).
[13] V. K. Jain and T. M. Srinivasan, Pramana **10**, 155 (1978).
[14] V. K. Jain, Z. Naturforsch. **33a**, 1389 (1978).
[15] V. K. Jain and P. Venkateswarlu, Ind. J. Pure Appl. Phys. **16**, 841 (1978); V. K. Jain and T. M. Srinivasan, Ind. J. Phys. **52A**, 85 (1978).
[16] R. E. Gerkin and D. L. Thorsell, J. Chem. Phys. **57**, 2665 (1972).
[17] A. Zalkin, J. D. Forrester, and D. H. Templeton, J. Chem. Phys. **39**, 2881 (1963).
[18] V. K. Jain, Z. Naturforsch. **32a**, 1364 (1977); V. K. Jain and P. Venkateswarlu, J. Chem. Phys. **70**, 5168 (1979).
[19] R. W. Wilkins and J. W. Culvahouse, Phys. Rev. **B 14**, 1830 (1976).
[20] W. Low and E. L. Offenbacher, Electron Spin Resonance of Magnetic Ions in Complex Oxides, Solid State Physics Vol. 17 (Academic Press New York, 1965), p. 135.
[21] V. K. Sharma, J. Chem. Phys. **54**, 496 (1971).
[22] T. Mitsuma, J. Phys. Soc. Japan **17**, 128 (1962).
[23] R. S. Saraswat and G. C. Upreti, J. Chem. Phys. **67**, 5428 (1977); J. Phys. Soc. Japan **44**, 1142 (1978).
[24] M. R. St. John, Ph. D. Thesis, University of California, Berkeley (1975).
[25] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford 1970, p. 535.
[26] B. Bleaney, R. J. Elliott, and H. E. D. Scovil, Proc. Phys. Soc. London A **64**, 933 (1951).
[27] R. E. Gerkin and W. J. Rogers, J. Chem. Phys. **68**, 504 (1978).